Chapter 19 ElectroChemistry

These Notes are to **SUPPLIMENT** the Text, They do NOT Replace reading the Text Material. **Additional material that is in the Text will be on your tests! To get the most information, READ THE CHAPTER** prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test!

The author is providing these notes as an addition to the students reading the text book and listening to the lecture. Although the author tries to keep errors to a minimum, the student is responsible for correcting any errors in these notes.

Pile Cell: Zinc and silver disks separated by paper disks soaked in NaCl.

Daniell Cell: Each metal was surrounded by a solution of the metal ion and the solutions were separated by a porous ceramic barrier.

Oxidation-Reduction half reactions:

Redox involves a transfer of electrons. For the above cells:

$$Zn \rightarrow Zn^{+2} + 2\ e^{-} \qquad\qquad Cu^{+2} + 2\ e^{-} \rightarrow Cu$$

Skeleton Redox Equations:

1. What species is oxidized?   What species is reduced?

2. What species results from the oxidation and reduction?
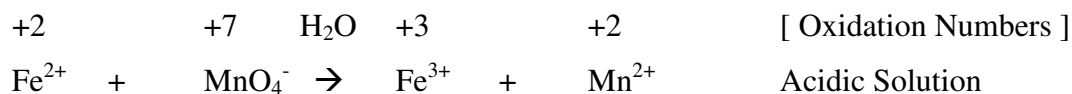
3. Does the reaction occur in acid or basic solution?

OXIDATION = Loss of electrons   **REDUCTION** = Gain of electrons

Oxidation Agent is reduced: $Cu^{+2} \rightarrow Cu^{o}$ **Reduction Agent is oxidized**

Iron (II) is oxidized to Iron (III) with permanganate ion which is reduced to manganese (II) ion:

+2		+7 H_2O	+3	+2	[Oxidation Numbers]
Fe^{2+}	+	$MnO_4^{-} \rightarrow$	Fe^{3+}	+ Mn^{2+}	Acidic Solution

# Balancing Redox Equations in Acidic Solutions:

1. Assign Oxidation Numbers to each atom so you can determine which atom is

oxidized [increases in ox number] and which is

reduced [decreases in ox number]. [See equation above]

2. Split the Skeleton Equation into two half reactions

Species that increases in oxidation number write as an oxidation half reaction
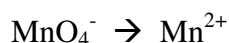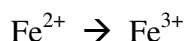
$Fe^{2+} \rightarrow Fe^{3+}$ [$Fe^{2+} \rightarrow Fe^{3+} + e^-$]

Species that decreases in oxidation number write as the reduction half reaction

$MnO_4^- \rightarrow Mn^{2+}$ [$MnO_4^- + 5 e^- \rightarrow Mn^{2+}$]
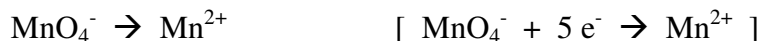
3. Complete and balance each half reaction:

A. Balance all atoms except for O and H

$Fe^{2+} \rightarrow Fe^{3+}$

$MnO_4^- \rightarrow Mn^{2+}$

B. Balance O atoms by adding H_2O to one side of the equation

$MnO_4^- \rightarrow Mn^{2+} + 4 H_2O$

C. Balance H atoms by adding H^+ ions to one side of the equation

$MnO_4^- + 8 H^+ \rightarrow Mn^{2+} + 4 H_2O$
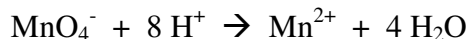
D. Balance the electric charge by adding e^- to the more positive side

$MnO_4^- + 8 H^+ + 5e^- \rightarrow Mn^{2+} + 4 H_2O$ Note e^- gained in a reduction

Fe^{2+} $\rightarrow Fe^{3+} + e^-$
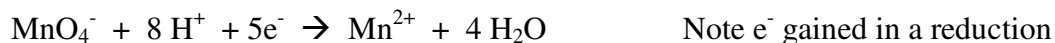
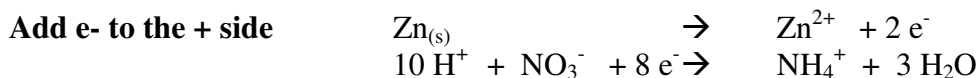**4. Combine the two half reactions to obtain the balanced Redox equation.**
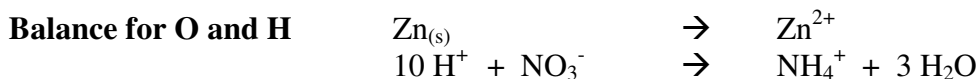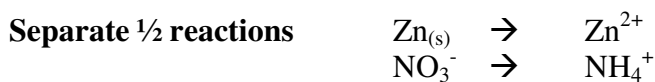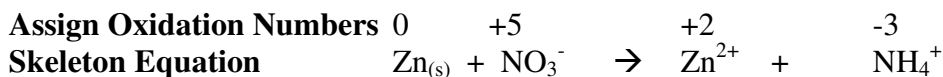
A. Multiply each half by a factor so when the ½ reactions are added the electrons cancel out

1 x   [$MnO_4^- + 8 H^+ + 5e^-$ $\rightarrow Mn^{2+} + 4 H_2O$]

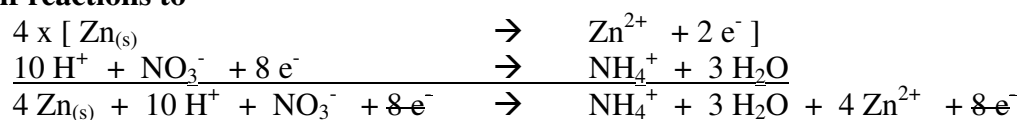5 x   [Fe^{2+} $\rightarrow Fe^{3+} + e^-$]
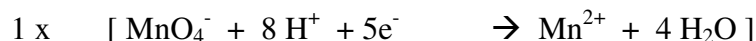
B. Simplify the balanced equation by canceling species that are on both sides of the equation and reduce the coefficients to the smallest whole numbers.

$5 Fe^{2+} + MnO_4^- + 8 H^+ + \cancel{5e^-} \rightarrow Mn^{2+} + 4 H_2O + 5 Fe^{3+} + \cancel{5e^-}$
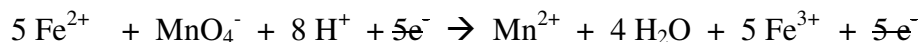
Example 19.1 Zinc metal reacts with nitric acid in concentrated solution to reduce the nitrate to ammonium and the zinc is oxidized to Zn^{2+}. Write the net ionic equation for this reaction?

Assign Oxidation Numbers 0   +5   +2   -3

Skeleton Equation $Zn_{(s)} + NO_3^- \rightarrow Zn^{2+} + NH_4^+$

Separate ½ reactions $Zn_{(s)} \rightarrow Zn^{2+}$
                                $NO_3^- \rightarrow NH_4^+$

Balance for O and H $Zn_{(s)} \rightarrow Zn^{2+}$
                                $10\,H^+ + NO_3^- \rightarrow NH_4^+ + 3\,H_2O$

Add e- to the + side $Zn_{(s)} \rightarrow Zn^{2+} + 2\,e^-$
                                $10\,H^+ + NO_3^- + 8\,e^- \rightarrow NH_4^+ + 3\,H_2O$

Combine the two half reactions to

           $4 \times [\ Zn_{(s)} \rightarrow Zn^{2+} + 2\,e^-\ ]$
           $\underline{10\,H^+ + NO_3^- + 8\,e^- \rightarrow NH_4^+ + 3\,H_2O}$
           $4\,Zn_{(s)} + 10\,H^+ + NO_3^- + \cancel{8\,e^-} \rightarrow NH_4^+ + 3\,H_2O + 4\,Zn^{2+} + \cancel{8\,e^-}$

Exercise 19.1 Iodine reacts with nitric acid to form HIO_3, the skeleton equation is:

     $I_{2(s)} + NO_3^- \rightarrow IO_3^- + NO_{2(g)}$ Show the complete Redox Equations

Assign oxidation numbers to the skeleton equation (Step 1).
     0   +5   +5   +4
     $I_2 + NO_3^- \rightarrow IO_3^- + NO_2$
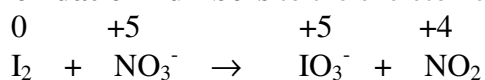
Separate into two incomplete half-reactions (Step 2).
Iodine is oxidized (increases in oxidation number), and nitrogen is reduced (decreases in oxidation number).
     $I_2 \rightarrow IO_3^-$ $NO_3^- \rightarrow NO_2$

Balance each half-reaction separately.
       The oxidation half-reaction is not balanced in I, so place a two in front of IO_3^- (Step 3a).
       Then add six H_2O's to the left side to balance O atoms (Step 3b), and
       add twelve H^+ ions to the right side to balance H atoms (Step 3c).
       Add ten electrons to the right side to balance the charge (Step 3d).
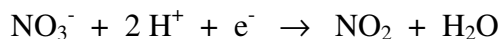The balanced oxidation half-reaction is

     $I_2 + 6\,H_2O \rightarrow 2\,IO_3^- + 12\,H^+ + 10\,e^-$

       The reduction half-reaction is balanced in N (Step 3a).
       Add one H_2O to the right side to balance O atoms (Step 3b), and
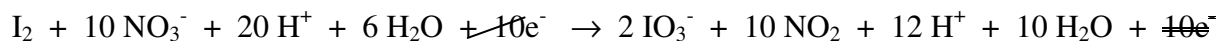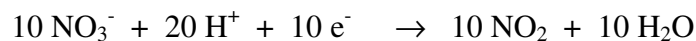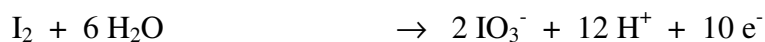   add two H^+ ion to the left side to balance H atoms.
       Finally, add one electron to the left side to balance the charge (Step 3d).
The balanced reduction half-reaction is

     $NO_3^- + 2\,H^+ + e^- \rightarrow NO_2 + H_2O$

Multiply the reduction half-reaction by ten so that, when added, the electrons cancel (Step 4a).

$$I_2 + 6 H_2O \rightarrow 2 IO_3^- + 12 H^+ + 10 e^-$$

$$10 NO_3^- + 20 H^+ + 10 e^- \rightarrow 10 NO_2 + 10 H_2O$$

$$I_2 + 10 NO_3^- + 20 H^+ + 6 H_2O + \cancel{10 e^-} \rightarrow 2 IO_3^- + 10 NO_2 + 12 H^+ + 10 H_2O + \cancel{10 e^-}$$

Simplify the equation by canceling the twelve H^+ and six H_2O that appear on both sides.
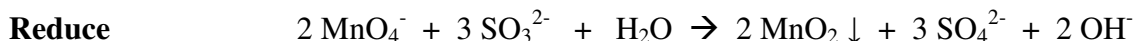The coefficients do not need to be reduced (Step 4b). The net ionic equation is

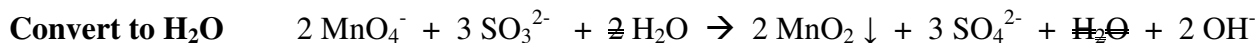$$I_2(s) + 10 NO_3^-(aq) + 8 H^+(aq) \rightarrow 2 IO_3^-(aq) + 10 NO_2(g) + 4 H_2O(l)$$
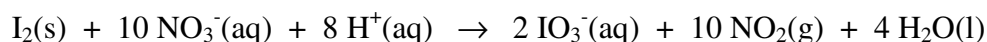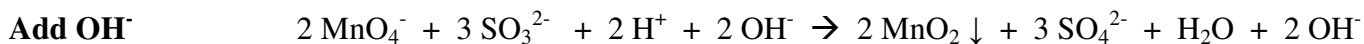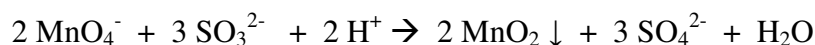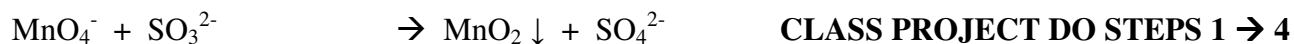
Balancing Redox Equations in Basic Solutions   Steps 1-4 above

5. Note the number of H^+ in the equation and put that number of OH^- on both sides of the equation

6. Change $H^+ + OH^- \rightarrow H_2O$,   Cancel H_2O's on both sides, Reduce equation to simplest terms

**Example 19.2** Permanganate ion oxidizes Sulfite in basic solution:

$$MnO_4^- + SO_3^{2-} \rightarrow MnO_2 \downarrow + SO_4^{2-} \qquad \textbf{CLASS PROJECT DO STEPS 1} \rightarrow \textbf{4}$$

$$2 MnO_4^- + 3 SO_3^{2-} + 2 H^+ \rightarrow 2 MnO_2 \downarrow + 3 SO_4^{2-} + H_2O$$

Add OH⁻ $2 MnO_4^- + 3 SO_3^{2-} + 2 H^+ + 2 OH^- \rightarrow 2 MnO_2 \downarrow + 3 SO_4^{2-} + H_2O + 2 OH^-$

Convert to H₂O $2 MnO_4^- + 3 SO_3^{2-} + \cancel{2} H_2O \rightarrow 2 MnO_2 \downarrow + 3 SO_4^{2-} + \cancel{H_2O} + 2 OH^-$

Reduce $2 MnO_4^- + 3 SO_3^{2-} + H_2O \rightarrow 2 MnO_2 \downarrow + 3 SO_4^{2-} + 2 OH^-$

Exercise 19.2 Balance the following in basic solution: $H_2O_2 + ClO_2 \rightarrow ClO_2^- + O_2$
After balancing the equation as if it were in acid solution, you obtain the following:

$$H_2O_2 + 2 ClO_2 \rightarrow 2 ClO_2^- + O_2 + 2 H^+$$

Add two OH^- to both sides of the equation (Step 5), and replace the two H^+ and two OH^- on the right side with
     two H_2O.
No further cancellation is required. The balanced equation for the reaction in basic solution is

$$H_2O_2 + 2 ClO_2 + 2 OH^- \rightarrow 2 ClO_2^- + O_2 + 2 H_2O$$
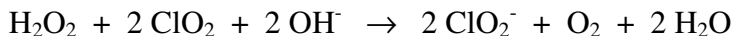
Voltaic Cells

Electrochemical Cell a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current

Voltaic / Galvanic Cell is an electrochemical cell in which a spontaneous reaction generates an electric current
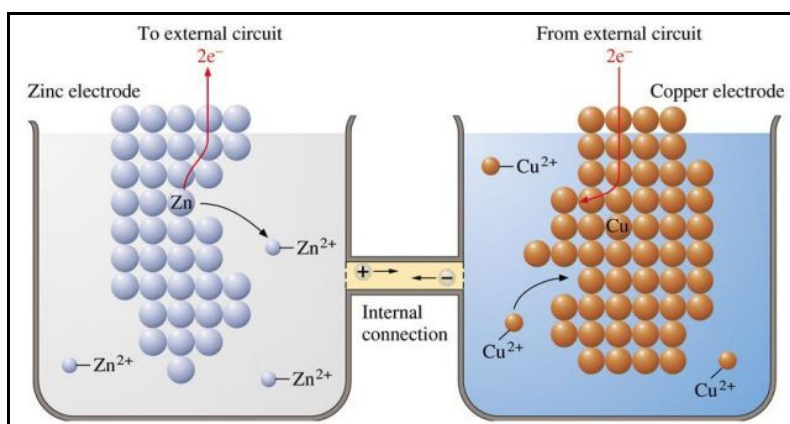
Electrolytic Cell is an electrochemical cell in which an electric current drives an otherwise non-spontaneous reaction/

19.2 Construction of Voltaic Cells

Voltaic cell consists of two half-cells that are each electrically connected.

Half-Cell is a portion of an electrochemical cell in which a half reaction takes place

Internal Connection allows ions to flow between the half cells without mixing of the half cell solutions.
Salt Bridge is a tube of an electrolyte in a gel that is connected to the two half-cells of a voltaic cell
[The Zinc Strip on the left is the Anode]
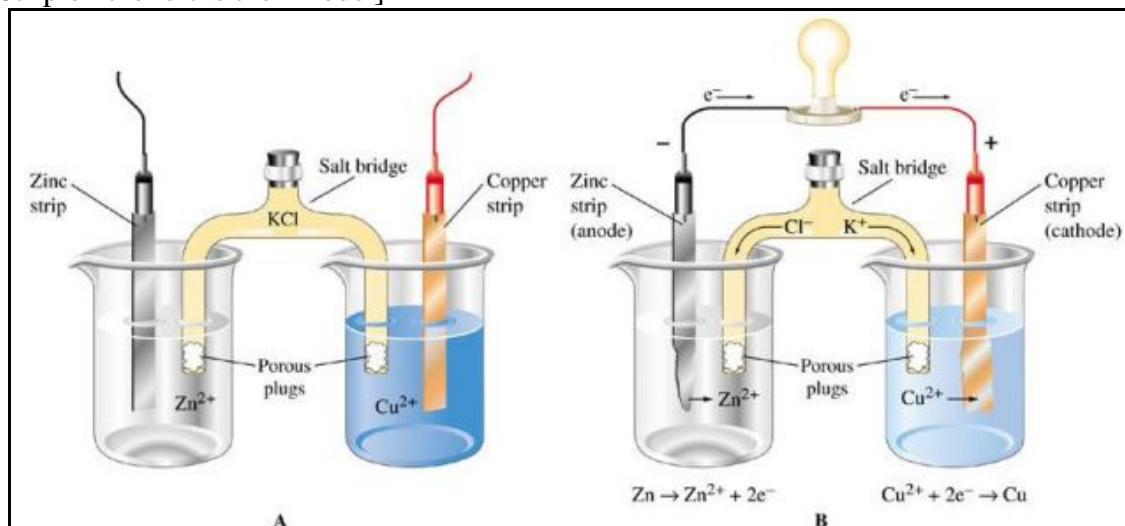
Example Zinc / Cu Voltaic Cell: $\quad$ Zn ↓ $\qquad$ → Zn^{2+} + 2 e$^-$ $\qquad$ [Oxidation]
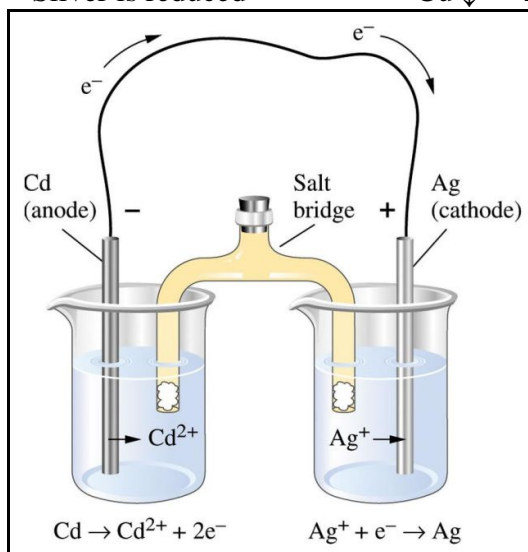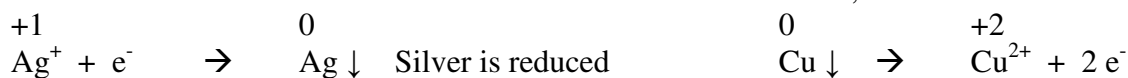$$Cu^{2+} + 2 e^- \rightarrow Cu ↓$$
Cell Reaction is the Net Reaction that occurs in a voltaic cell.
Sum of the half reactions: $\qquad$ Zn ↓ + Cu^{2+} → Zn^{2+} + Cu ↓
Note: The anode in a voltaic cell has a negative sign.

Example 19.3 Draw the voltaic cell that has Cd rod in $Cd(NO_3)_2$ and a Ag rod in $AgNO_3$, connected by a salt bridge. Label the anode and cathode and show all the chemical reactions, silver is reduced.
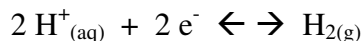
$$\begin{array}{ccccccc} +1 & & & 0 & & 0 & & +2 \\ Ag^+ + e^- & \rightarrow & Ag\downarrow & \text{Silver is reduced} & & Cu\downarrow & \rightarrow & Cu^{2+} + 2\,e^- \end{array}$$

19.3 Notation for Voltaic Cells

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \qquad \parallel \qquad Cu^{2+}_{(aq)} \mid Cu_{(s)}$$

anode   **salt bridge**   **cathode**
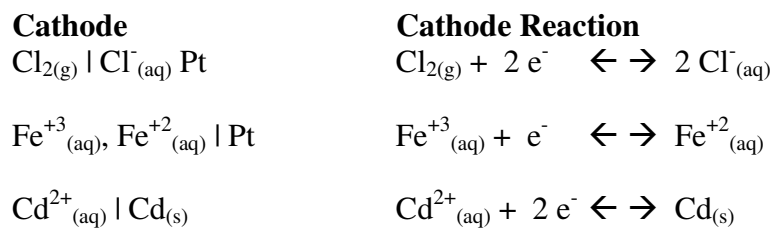
Anode = Oxidation half-cell = on Left

Notation: $_{(s)}$ is for the actual **cell terminals** and are at the end

Gas half-reaction, where the terminal is inert such as Platinum, a Hydrogen Electrode is H_2 bubbles over a platinum plate: $\qquad\qquad 2\,H^+_{(aq)} + 2\,e^- \leftrightarrow H_{2(g)}$

Notation: **Cathode:** $H^+_{(aq)} \mid H_{2(g)}\,Pt$ **Anode:** $Pt \mid H_{2(g)}\,H^+_{(aq)}$

Other Examples:

Cathode	**Cathode Reaction**
$Cl_{2(g)} \mid Cl^-_{(aq)}\,Pt$	$Cl_{2(g)} + 2\,e^- \leftrightarrow 2\,Cl^-_{(aq)}$
$Fe^{+3}_{(aq)}, Fe^{+2}_{(aq)} \mid Pt$	$Fe^{+3}_{(aq)} + e^- \leftrightarrow Fe^{+2}_{(aq)}$
$Cd^{2+}_{(aq)} \mid Cd_{(s)}$	$Cd^{2+}_{(aq)} + 2\,e^- \leftrightarrow Cd_{(s)}$

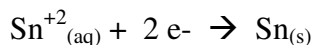**Exercise 19.4** Write the notation for: $2H^+_{(aq)} + 2\,e^- \leftrightarrow H_{2(g)}$ $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\,e^-$

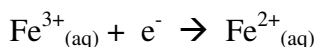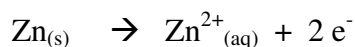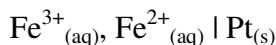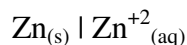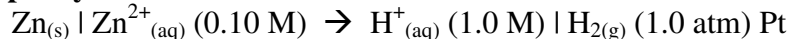$$Zn(s) \mid Zn^{2+}(aq) \parallel H^+(aq) \mid H_2(g) \mid Pt(s).$$
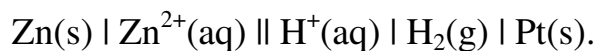
Write the Cell Reaction from the Cell Notation

Example 19.4 Write the cell reaction for a voltaic cell: $Tl_{(s)} \mid Tl^+_{(aq)} \parallel Sn^{+2}_{(aq)} \mid Sn_{(s)}$

$Tl_{(s)} \mid Tl^+_{(aq)}$ $\qquad\qquad\qquad\qquad$ $Sn^{+2}_{(aq)} \mid Sn_{(s)}$

$Tl_{(s)} \rightarrow Tl^+_{(aq)} + e^-$ $\qquad\qquad$ $Sn^{+2}_{(aq)} + 2\ e- \rightarrow Sn_{(s)}$

$2\ Tl_{(s)} \rightarrow Tl^+_{(aq)} + 2\ e^-$ $\qquad\qquad$ $Sn^{+2}_{(aq)} + 2\ e- \rightarrow Sn_{(s)}$

$2\ Tl_{(s)} + Sn^+_{(aq)} \rightarrow 2\ Tl^+_{(aq)} + Sn_{(s)}$
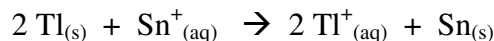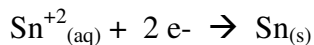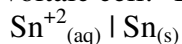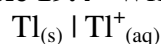
For the voltaic cell: $\quad Zn_{(s)} \mid Zn^{+2}_{(aq)} \parallel Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)} \mid Pt_{(s)}$

$Zn_{(s)} \mid Zn^{+2}_{(aq)}$ $\qquad\qquad\qquad\qquad$ $Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)} \mid Pt_{(s)}$

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\ e^-$ $\qquad\qquad$ $Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$

$Zn_{(s)} + 2\ Fe^{3+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2\ Fe^{2+}_{(aq)}$
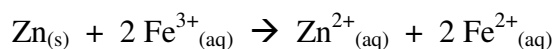
Must specify the concentrations of the solutions / ions:

$Zn_{(s)} \mid Zn^{2+}_{(aq)} (0.10\ M) \rightarrow H^+_{(aq)} (1.0\ M) \mid H_{2(g)} (1.0\ atm)\ Pt$

Exercise 19.5 Give the cell reaction for the voltaic cell: $Cd_{(s)} \mid Cd^{+2}_{(aq)} \parallel H^+_{(aq)} \mid H_{2(g)} \mid Pt_{(s)}$

Class Project

$Cd(s) \rightarrow Cd^{2+}(aq) + 2\ e-$ $\qquad\qquad$ $2H^+(aq) + 2\ e- \rightarrow H_2(g)$
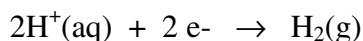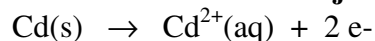
Summing the half-cell reactions gives the overall cell reaction.

$Cd(s) + 2H^+(aq) \rightarrow Cd^{2+}(aq) + H_2(g)$
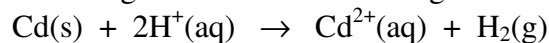
19.4 Electromotive Force

Work is needed to move the electrons in the wire or to move the ions through a solution.

Potential Difference is the difference in electric potential between two points.

Volt, V is the SI unit of potential difference

Electrical Work	=	Charge * potential difference
W		**-nF** $\quad$ *** V**
Joules	=	**coulombs * volts** $\quad$ 1 coulomb = 6.24×10^{18} elementary charges

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ 1 ampere is 1 coulomb of electrons per second

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ 1 Volt Coulomb = 1 Joule

Faraday constant, **F** is the magnitude of charge on one mole of electrons $\qquad$ **F = 96,500 C/mol e⁻**

Cells have resistance [e.g. the salt bridge] where it takes work to move the ions across it. The greater the current, the lower the voltage.

Electromotive Force, emf or cell potential (**E_{cell}**) is the maximum difference between the electrodes of a voltaic cell

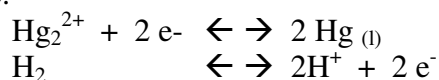**Anode** = negative pole, **Cathode** = positive pole

Maximum work (w_{max}) from a cell is related to the number of moles of e⁻ transferred (n) in cell equation.

$$\mathbf{w_{max} = -n\ F\ E_{cell}} \quad \text{n= \#moles of e-, \quad F = Faraday Const, \quad E_{cell} = cell emf}$$

Example 19.5 The emf of a cell is 0.650 v, what is the w_{max} when 0.500 g of H_2 is consumed?

$$Hg_2^{2+} + H_2 \leftarrow\rightarrow 2\ Hg_{(l)} + 2H^+$$
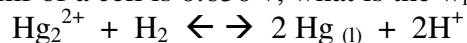
The half reactions are:

$$Hg_2^{2+} + 2\ e^- \leftarrow\rightarrow 2\ Hg_{(l)}$$
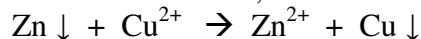$$H_2 \qquad\quad \leftarrow\rightarrow 2H^+ + 2\ e^-$$

n = 2 moles of electrons transferred

$$w_{max} = -n\ F\ E_{cell} = -2\ \text{mole e}^- \ *\ 96{,}500\ C/\text{mole e}^- \ *\ 0.650\ v = -1.25\ x\ 10^5\ v\ C = J$$

Now for 0.500 g of H_2: $\dfrac{0.500\ g\ H_2}{2.02\ g\ H_2/Mole} \quad *\ \dfrac{-1.25\ x\ 10^5\ J}{1\ \text{mole } H^2} = -3.09\ x\ 10^4\ J$

Exercise 19.6 The emf of a cell is 1.10 v, what is the w_{max} when 6.54 g of Zn is consumed?

$$Zn\downarrow + Cu^{2+} \rightarrow Zn^{2+} + Cu\downarrow$$

The half-reactions are

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

n equals two, and the maximum work for the reaction as written is

$$w_{max} = -nFE_{cell} = -2\ x\ 9.65\ x\ 10^4\ C/\text{mol e}^-\ x\ 1.10\ V = -2.1\underline{2}3\ x\ 10^5\ V{\cdot}C = -2.12\ x\ 10^5\ J$$

For 6.54 g of zinc metal, the maximum work is

$$6.54\ g\ Zn\ x\ \dfrac{1\ mol\ Zn}{65.39\ g\ Zn}\ x\ \dfrac{-2.123\ x\ 10^5\ J}{1\ mol\ Zn} = -2.1\underline{2}3\ x\ 10^4 = -2.12\ x\ 10^4\ J$$

19.5 Standard Cell emf

Cell emf is the measure of the cell driving force = E_{cell} = oxidation potential + reduction potential

Reduced species	$\rightarrow$ oxidized species + ne$^-$	oxidation at the anode
Oxidized species + ne$^-$	$\rightarrow$ reduced species	reduction at the cathode
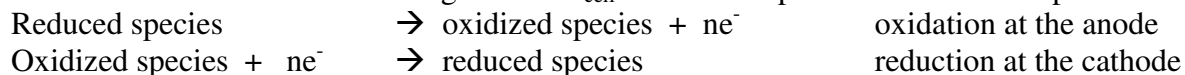
Oxidation potential for a ½ reaction = - Reduction potential for the REVERSE of the ½ reaction

The emf of a voltaic cell depends on the concentrations and temperatures of the substances

Standard emf = E^o_{cell} is the emf of a voltaic cell operating under standard state conditions [concentrations = 1 M, gas pressure = 1 atm, temp = 25 ^oC]

*** Standard Hydrogen Electrode is assigned a potential of 0.0 v.

*** Standard Electrode Potential = E^o at standard state conditions [concentrations = 1 M, gas pressure = 1 atm, temp = 25 ^oC]
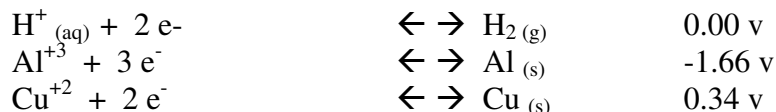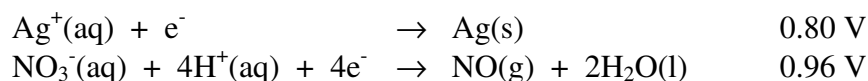
Strongest Reducing Agents have the most negative E^o

$$L^{+\ (aq)} + e^- \rightarrow Li_{(s)} \qquad Li_{(s)} \text{ is a strong reducer}$$
$$F_{2\ (g)} + 2\ e^- \rightarrow 2\ F^- \qquad F_2 \text{ is a strong oxidizer}$$

Example 19.6 Order the following **oxidizing agents** by increasing strength: Cl_2, H_2O_2, Fe^{3+}

$Cl_2 + 2$ e-	← →	$2 Cl^-$	1.36 v
$H_2O_2 + 2 H^+ + 2$ e-	← →	$2 H_2O$	1.78 v
$Fe^{3+} + e^-$	← →	Fe^{2+}	0.77 v
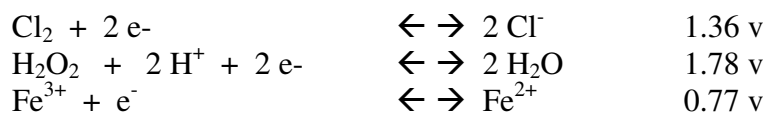
Order the following **reducing agents** by increasing strength: $H_{2 (g)}$, $Al_{(s)}$, $Cu_{(s)}$

$H^+_{(aq)} + 2$ e-	← →	$H_{2 (g)}$	0.00 v
$Al^{+3} + 3 e^-$	← →	$Al_{(s)}$	-1.66 v
$Cu^{+2} + 2 e^-$	← →	$Cu_{(s)}$	0.34 v

Exercise 19.7 What is he stronger oxidizing agent: $NO_3^-{}_{(aq)}$ in acidic solution going to NO, or $Ag^+{}_{(aq)}$

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad\qquad 0.80 \text{ V}$$
$$NO_3^-(aq) + 4H^+(aq) + 4e^- \rightarrow NO(g) + 2H_2O(l) \qquad 0.96 \text{ V}$$
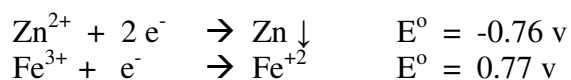
The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so NO_3^- is the stronger oxidizing agent.

Reaction Spontaneity: If the stronger oxidizing agent is the reactant the equation is spontaneous.
If the stronger reducing agent is the product, the reaction is spontaneous.

Example 19.7 Is the following spontaneous: $Zn^{2+} + 2 Fe^{2+} \rightarrow Zn \downarrow + 2 Fe^{3+}$
The ½ reactions:
$$Zn^{2+} + 2 e^- \rightarrow Zn \downarrow \qquad E^o = -0.76 \text{ v}$$
$$Fe^{3+} + e^- \rightarrow Fe^{+2} \qquad E^o = 0.77 \text{ v}$$
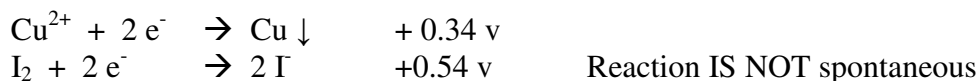
The stronger oxidizing agent is the more positive one.
Fe^{3+} is the stronger oxidizing agent, the reaction is non-spontaneous.

Exercise 19.8 Is the following spontaneous: $Cu^{2+} + 2 I^- \rightarrow Cu \downarrow + I_2$

$$Cu^{2+} + 2 e^- \rightarrow Cu \downarrow \qquad + 0.34 \text{ v}$$
$$I_2 + 2 e^- \rightarrow 2 I^- \qquad +0.54 \text{ v} \qquad \text{Reaction IS NOT spontaneous}$$
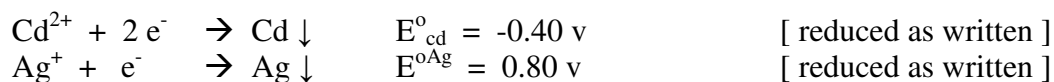
Strong Reducer

Standard Electrode (Reduction) Potentials in Aqueous Solution at 25°C*

Cathode (Reduction) Half-Reaction	Standard Potential, $E°(V)$
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.04
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.38
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.41
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.23
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$Fe^{3+}(aq) + 3e^- \rightleftharpoons Fe(s)$	−0.04
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	0.16
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	0.34
$IO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons I^-(aq) + 2OH^-(aq)$	0.49
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	0.52
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	0.77
$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	0.80
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg(l)$	0.85
$ClO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons Cl^-(aq) + 2OH^-(aq)$	0.90
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	0.90
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	0.96
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	1.07
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	1.49
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	1.78
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	2.01
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	2.87

Strong oxidizer

Cell emfs by addition of the ½ reaction and the standard potentials.

Here's a cell with Cadmium and Silver electrodes:

$$Cd^{2+} + 2\ e^- \rightarrow Cd\downarrow \qquad E^o_{cd} = -0.40\ v \qquad [\ reduced\ as\ written\ ]$$
$$Ag^+ + e^- \rightarrow Ag\downarrow \qquad E^{oAg} = 0.80\ v \qquad [\ reduced\ as\ written\ ]$$
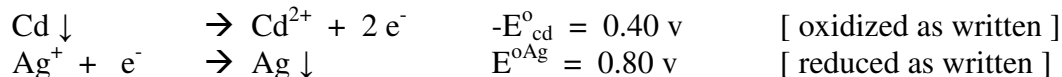
The cell is spontaneous with the stronger oxidation part on the left,
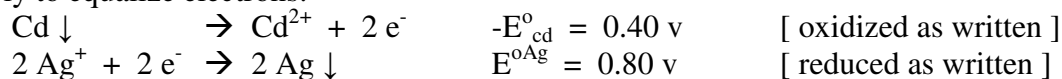**Ag^+ is a stronger oxidizing agent than Cd.**
You change the order and the sign of the most negative
So the reactions are:

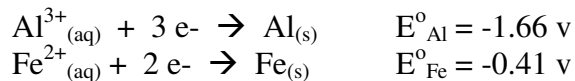$$Cd\downarrow \qquad\quad \rightarrow Cd^{2+} + 2\ e^- \qquad -E^o_{cd} = 0.40\ v \qquad [\ oxidized\ as\ written\ ]$$
$$Ag^+ + e^- \rightarrow Ag\downarrow \qquad E^{oAg} = 0.80\ v \qquad [\ reduced\ as\ written\ ]$$

Multiply to equalize electrons:

$$Cd\downarrow \qquad\quad \rightarrow Cd^{2+} + 2\ e^- \qquad -E^o_{cd} = 0.40\ v \qquad [\ oxidized\ as\ written\ ]$$
$$2\ Ag^+ + 2\ e^- \rightarrow 2\ Ag\downarrow \qquad E^{oAg} = 0.80\ v \qquad [\ reduced\ as\ written\ ]$$

$$Cd\downarrow + 2\ Ag^+ \rightarrow Cd^{2+} + 2\ Ag\downarrow \quad E^o = \sum E^o = 0.40\ v + 0.80\ v = 1.20\ v$$

A positive emf shows the cell reaction IS SPONTANEOUS.

$$E^o = E^o_{Cathode}\ E^o_{Anode}$$

Example 19.8 Calculate the standard emf of: $Al_{(s)} \mid Al^{3+}_{(aq)} \parallel Fe^{2+}_{(aq)} \mid Fe_{(s)}$
From equation Left is anode or the Oxidation ½ cell

$$Al^{3+}_{(aq)} + 3\ e^- \rightarrow Al_{(s)} \qquad E^o_{Al} = -1.66\ v$$
$$Fe^{2+}_{(aq)} + 2\ e^- \rightarrow Fe_{(s)} \qquad E^o_{Fe} = -0.41\ v$$

Change the direction and sign of the most negative

$$Al_{(s)} \qquad\qquad \rightarrow Al^{3+}_{(aq)} + 3\ e^- \qquad E^o_{Al} = +1.66\ v$$
$$Fe^{2+}_{(aq)} + 2\ e^- \rightarrow Fe_{(s)} \qquad\qquad E^o_{Fe} = -0.41\ v$$
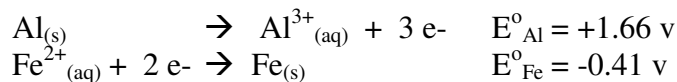
Multiply to cancel out the electrons

$$2 * [\ Al_{(s)} \qquad\qquad \rightarrow Al^{3+}_{(aq)} + 3\ e^-\ ]\ E^o_{Al} = +1.66\ v$$
$$3 * [\ Fe^{2+}_{(aq)} + 2\ e^- \rightarrow Fe_{(s)} \qquad] \qquad E^o_{Fe} = -0.41\ v$$

$$2\ Al_{(s)} + 3\ Fe^{2+}_{(aq)} \rightarrow 2\ Al^{3+}_{(aq)} + 3\ Fe_{(s)}\ \mathbf{E^o = \sum E^o = 1.25\ v}$$
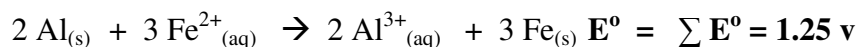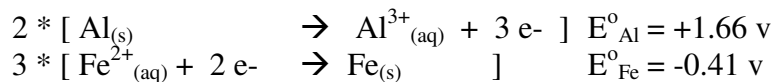
Or $E^o_{cell} = E^o_{Cathode} - E^o_{Anode} = -0.41\ v - (-1.66v) = 1.25\ v$

Exercise 19.9 Calculate E°_{cell} for $Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$

$Zn^{2+}(aq) + 2 e- \quad \rightarrow Zn(s); \qquad E^{\circ}_{Zn} = -0.76 \text{ V}$
$Cu^{2+}(aq) + 2 e- \quad \rightarrow Cu(s); \qquad E^{\circ}_{Cu} = 0.34 \text{ V}$
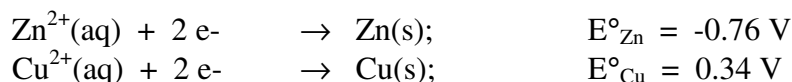
Reverse the first half-reaction and its half-cell potential to obtain

$Zn(s) \qquad\qquad\qquad \rightarrow Zn^{2+}(aq) + 2 e-; -E^{\circ}_{Zn} = 0.76 \text{ V}$
$Cu^{2+}(aq) + 2 e- \quad \rightarrow Cu(s); \qquad E^{\circ}_{Cu} = 0.34 \text{ V}$
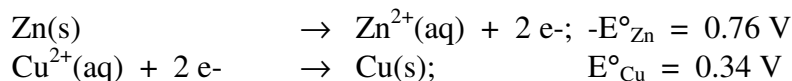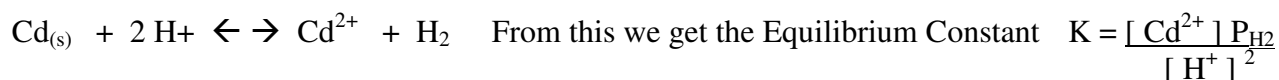
Obtain the cell emf by adding the half-cell potentials.

$E^{\circ}_{cell} = E^{\circ}_{Cu} - E^{\circ}_{Zn} = 0.34 \text{ V} + 0.76 \text{ V} = 1.10 \text{ V}$

19.6 Equilibrium Constants from emfs   SKIP THIS SECTION

## 19.7 Dependence of emf on Concentration

Nernst Equation: When the concentrations are not at the **Standard emf = E°_{cell}** then use this equation:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} * \text{Log q}$$

$Cd_{(s)} \mid Cd^{2+} (0.0100M) \parallel H^{+} (1.00 \text{ M}) \mid H_2 (1.00 \text{ atm}) \text{ Pt}$

$Cd_{(s)} + 2 H+ \leftarrow\rightarrow Cd^{2+} + H_2$ From this we get the Equilibrium Constant $K = \dfrac{[Cd^{2+}] P_{H2}}{[H^{+}]^2}$

and we calculate $Q = \dfrac{[Cd^{2+}] P_{H2}}{[H^{+}]^2} = \dfrac{0.0100 * 1.00}{(1.00)^2} = \quad 0.0100$

Example 19.12 What is the emf of $Zn_{(s)} \mid Zn^{2+} (1.00 \times 10^{-5}M) \parallel Cu^{2+} (0.100 \text{ M}) \mid Cu_{(s)}$, The standard emf is 1.10 v.
The cell Reaction is: $Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+} + Cu_{(s)}$
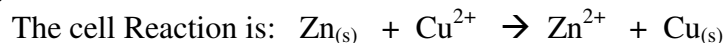
$Q = \dfrac{[Zn^{2+}]}{[Cu^{2+}]} = \dfrac{1.00 \times 10^{-5}}{0.100} = 1.00 \times 10^{-4}$

$E_{cell} = E^{\circ}_{cell} - \dfrac{0.0592}{N} * \text{Log q} = 1.10 - \dfrac{0.0592}{2} \log (1.00 \times 10^{-4}) = 1.10 - (-0.12) = 1.22 \text{ v}$

Exercise 19.13   What is the emf of $Zn_{(s)} \mid Zn^{2+} (0.200 \text{ M}) \parallel Ag^{+} (0.00200 \text{ M}) \mid Ag_{(s)}$

$Zn(s) \qquad\qquad\qquad \rightarrow \quad Zn^{2+}(aq) + 2 e- \qquad -E^{\circ} = 0.76 \text{ V}$
$2 Ag^{+}(aq) + 2 e- \quad \rightarrow \quad 2 Ag(s) \qquad\qquad E^{\circ} = 0.80 \text{ V}$

$Zn(s) + 2 Ag^{+}(aq) \quad \rightarrow \quad Zn^{2+}(aq) + 2Ag(s) \quad E^{\circ}_{cell} = 1.56 \text{ V}$
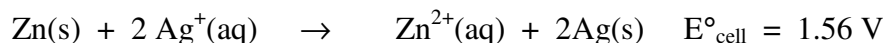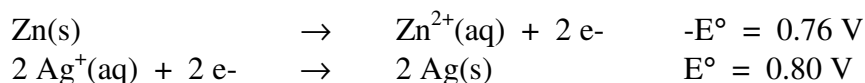
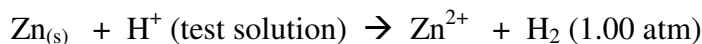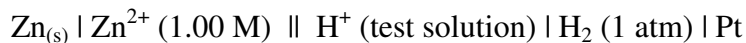Note that n equals two. The reaction quotient is

$Q = \dfrac{[Zn^{2+}]}{[Ag^{+}]^2} = \dfrac{0.200}{(0.00200)^2} = 5.0\underline{0} \times 10^{4}$

The standard emf is 1.56 V, so the Nernst equation becomes

$$E_{cell} = E°_{cell} - \frac{0.0592}{n}\log Q = 1.56 - \frac{0.0592}{2}\log(5.00 \times 10^4) = 1.56 - 0.13\underline{9}09 = 1.4\underline{2}09 = 1.42 \text{ V}$$

The pH Meter: pH is determined using the Nernst equation.

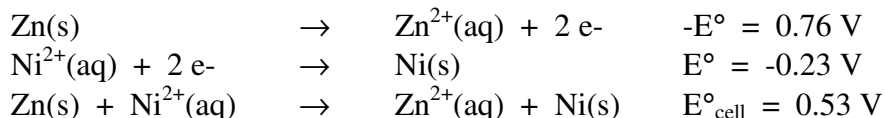A Zinc, Zn+ electrode is connected to a Hydrogen electrode using the test solution.

$$Zn_{(s)} \mid Zn^{2+} (1.00 \text{ M}) \parallel H^+ \text{ (test solution)} \mid H_2 \text{ (1 atm)} \mid Pt$$

$$Zn_{(s)} + H^+ \text{ (test solution)} \rightarrow Zn^{2+} + H_2 (1.00 \text{ atm})$$

$$Q = \frac{[Zn^{2+}]\, P_{H2}}{[H^+]^2} = \frac{1.00}{[H^+]^2}$$

$$E_{cell} = E_{cell} - \frac{0.0592}{N} * \text{Log } q = 1.10 - \frac{0.0592}{2}\log\left(\frac{1}{[H^+]^2}\right) \qquad \text{And since pH} = -\log[H^+]$$

$$pH = 0.76 - E_{cell} / 0.0592 \qquad \text{The pH is measured with a volt meter!}$$

As the Hydrogen electrode is difficult to use in a lab, a Glass Electrode [silver wire coated with silver chloride immersed in dilute HCl with a thin glass membrane to separate it from the test solution] and a Calomel Electrode [Mercury – mercury (I) chloride electrode] are used!

Exercise 19.14 What is the Nickel (II) ion concentration in: $Zn_{(s)} \mid Zn^{2+} (1.00 \text{ M}) \parallel Ni^{2+}_{(aq)} \mid Ni_{(s)}$

$$
\begin{array}{llll}
Zn(s) & \rightarrow & Zn^{2+}(aq) + 2\text{ e-} & -E° = 0.76 \text{ V} \\
Ni^{2+}(aq) + 2\text{ e-} & \rightarrow & Ni(s) & E° = -0.23 \text{ V} \\
Zn(s) + Ni^{2+}(aq) & \rightarrow & Zn^{2+}(aq) + Ni(s) & E°_{cell} = 0.53 \text{ V}
\end{array}
$$

Note that n equals two. The standard emf is 0.53 V, and the emf is 0.34 V, so the Nernst equation becomes

$$E_{cell} = E°_{cell} - \frac{0.0592}{n}\log Q \qquad 0.34 \text{ V} = 0.53 \text{ V} - \frac{0.0592}{2}\log Q$$

Rearrange and solve for log Q $\qquad \log Q = \frac{2}{0.0592} \times (0.53 - 0.34) = 6.\underline{4}18$

Take the antilog of both sides $\qquad Q = \frac{[Zn^{2+}]}{[Ni^{2+}]} = \text{antilog } (6.418) = \underline{2}.623 \times 10^6$

Substitute in $[Zn^{2+}] = 1.00$ M and solve for $[Ni^{2+}]$. $\qquad \frac{1.00 \text{ M}}{[Ni^{2+}]} = 2.624 \times 10^6$

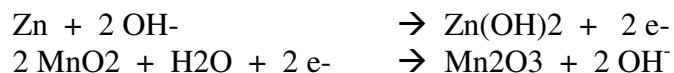$[Ni^{2+}] = \underline{3}.81 \times 10^{-7} = 4 \times 10^{-7} \text{ M}$

19.8 Commercial Voltaic Cells

Zinc-Carbon or dry cell   1.5 v
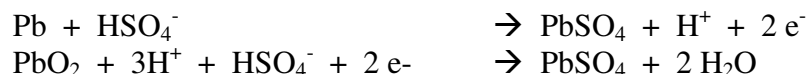>   Zinc can as the anode, graphite rod in the center, past of magnesium dioxide and ammonium

$$Zn \rightarrow Zn^{+2} + 2 \text{ e-}$$
$$2 NH_4^+ + 2 MnO_2 + 2 \text{ e-} \rightarrow Mn_2O_3 + H_2O + 2 NH_3$$
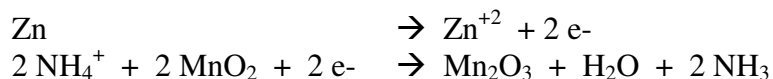
Alkaline dry cell   Same but use KOH in place of ammonium chloride

$$Zn + 2 OH- \rightarrow Zn(OH)2 + 2 \text{ e-}$$
$$2 MnO2 + H2O + 2 \text{ e-} \rightarrow Mn2O3 + 2 OH^-$$

Lithium-Iodine Battery

Lead storage cell   Lead alloy grids, and lead dioxide

$$Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2 \text{ e}^-$$
$$PbO_2 + 3H^+ + HSO_4^- + 2 \text{ e-} \rightarrow PbSO_4 + 2 H_2O$$

Nickel-cadmium cell anode of cadium, cathode nickel oxide hydrate in KOH

$$Cd + 2 OH^- \rightarrow Cd(OH)_2 + 2 \text{ e}^-$$
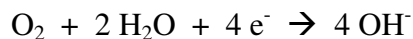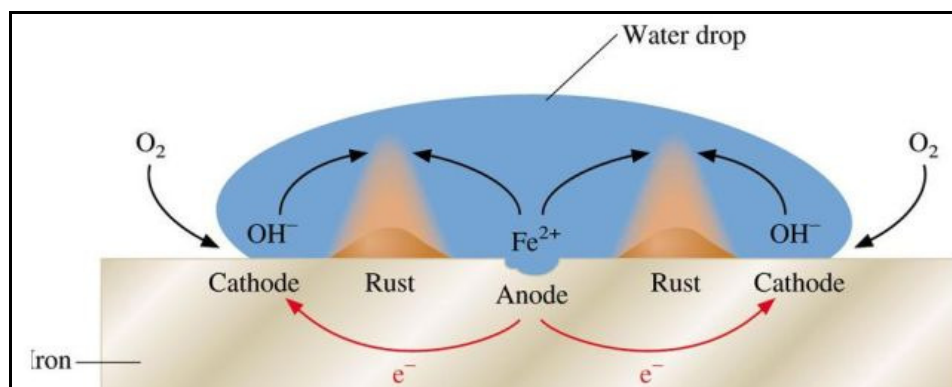$$NiOOH + H_2O + \text{ e-} \rightarrow Ni(OH)_2 + OH^-$$
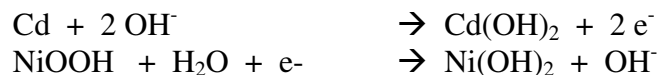
Fuel Cell   operates in a continuous mode, as reactants are there, it runs

$$H_2 \rightarrow 2 H^+ + 2 \text{ e}^-$$
$$O_2 + 4 H^+ + 4 \text{ e}^- \rightarrow 2 H_2O$$
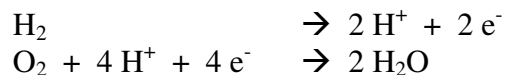
Rusting from a drop of water – the electrochemical process of rusting iron

$$O_2 + 2 H_2O + 4 \text{ e}^- \rightarrow 4 OH^- \qquad Fe \rightarrow Fe^{2+} + 2 \text{ e-}$$

$$Fe^{+2} + 2 OH^- \rightarrow Fe(OH)_2 \qquad 4 Fe(OH)_2 + O_2 \rightarrow 2 Fe_2O_3 + H_2O$$
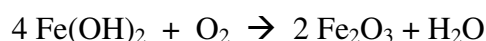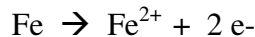
Cathodic Protection – Magnesium is a more "Active Metal" [more electropositive] and will react in place of Iron:

Magnesium Rod   Mg $\rightarrow$ Mg^{2+} + 2 e^- Instead of   Fe $\rightarrow$ Fe^{+2} + 2 e^-
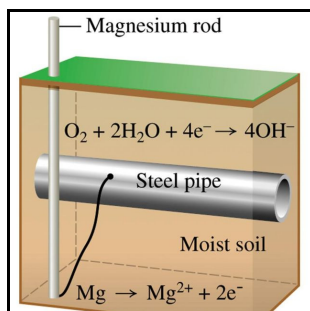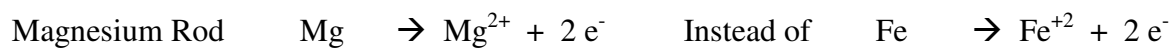
19.9 Electrolysis of Molten Salts

Molten Sodium Chloride 801 ^{o}C.

Na^+ + e- $\rightarrow$ Na Cl^- $\rightarrow$ ½ Cl2 + e-

19.10 Aqueous Electrolysis

Electrolysis of Sulfuric Acid

Electrolysis of Sodium Chloride Solutions

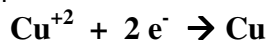Electrolysis of dilute NaCl gives H^2 and O^2

More concentrated solutions gives H^2 and Cl^2 and OH^-
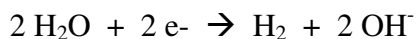
Chlor-Alkali Membrane Cell

Electroplating of Metals

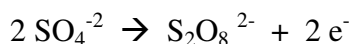Ex 19.13   Electrolysis of CuSO4
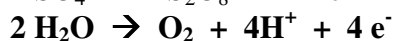
     CATHODE REACTIONS $Cu^{+2} + 2 e^- \rightarrow Cu$ **Eo = 0.34 v**

                                       $2 H_2O + 2 e^- \rightarrow H_2 + 2 OH^-$ Eo = - 0.83 v

As Copper is larger than water, the Cu+2 is reduced

     ANODE REACTIONS $2 SO_4^{-2} \rightarrow S_2O_8^{\ 2-} + 2 e^-$ -Eo = - 2.01 v

                                        $\mathbf{2 H_2O \rightarrow O_2 + 4H^+ + 4 e^-}$ **-Eo = -1.23 v**

Water is the more positive value

Exercise 19.16 Elecrolyze silver nitrate, give the ½ reactions

     Ag+ + e- $\rightarrow$ Ag $E^o = 0.80v$
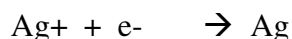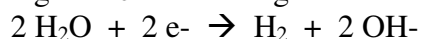
     $2 H_2O + 2 e^- \rightarrow H_2 + 2 OH^-$ $E^o = - 0.83$ v

Silver E^o is more positive, so silver is plated out

     $Ag^+ + e^- \rightarrow$ Ag $2 H_2O \rightarrow O_2 + 4H^+ + 4e^-$
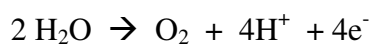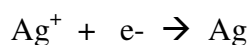
Stoichiometry of Electrolysis

One Faraday (9.65×10^4 C) = one mole of electrons

Ampere (A) is the base unit of current in the SI system. The Coulomb (C) is an ampere – second.

Example 19.14   You need to know how to do this

     Moles * Number of electrons * $\dfrac{9.65 \times 10^4 \text{ C}}{1 \text{ mole e-}}$ =   Coul   (C = coulomb)

     Current = charge (C) / time = Amp

Example 19.15   You need to know how to do this

Exercise 19.18 How many grams of O_2 come from the electrolysis of water with 0.0565 A for 1.85×10^4 sec.? When the current flows for 1.85×10^4 s, the amount of charge is

     0.0565 A x 1.85×10^4 s = $1.0\underline{45} \times 10^3$ C

Note that four moles of electrons are equivalent to one mol of O_2. Hence,

     1.045×10^3 C x $\dfrac{1 \text{ mol e}^-}{9.65 \times 10^4 \text{ C}}$ x $\dfrac{1 \text{ mol } O_2}{4 \text{ mol e}^-}$ x $\dfrac{32.00 \text{ g } O_2}{1 \text{ mol } O_2}$

               = $0.086\underline{65}$ = 0.0866 g O_2

Chem 1046, Ch 20 Test Questions [does not include the list for Titration and Ch 18]
Potential Test Questions:
The final updated Chapter 20 Electochemistry Lecture Notes are now posted.
As I may have forgotten to give some example test question numbers, Ch 19 potential math questions are
summarized below:

1. Balancing Redox equations in acidic solutions
2. Balancing Redox equations in basic solutions
3. Example 19.3 Draw the voltaic cell
4. 19.3 Notation for voltaic cells
5. Example 19.4 Write the cell reaction for
6. Exercise 19.5 Give the cell reaction for
7. Example 19.5
8. Exercise 19.6
9. Example 19.8
10. Exercise 19.9
11. Exercise 19.13
12. 19.8 Commercial Voltaic Cells
13. Rusting from a drop of water

And any bold defs are fair game.