

Ch. 19 Electrochemistry and its Applications

- electron flow = electricity
 - electrochemistry = the study of electron transfer
 - “reduction” and “oxidation” (“redox”) chemistry is central
1. Product-favored redox reactions run batteries
 2. Voltmeters quantify electrochemistry
 - measure reactivity of redox reactions
 3. Reactant-favored redox reactions can be pushed to product side by external electricity
 - “Electrolysis”
 - Electrolysis is the source of many pure metals and other not found in nature (“Electroplating”)

$$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr} \quad (\text{chrome-plating})$$
 4. One can also force oxidation reactions under the appropriate conditions

$$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \quad (\text{for disinfecting water})$$
 5. “Corrosion”, “rusting” are redox processes that are undesirable and that we need to prevent

Assigning Oxidation Numbers (See Section 5.4)

This is a more complete set of rules than your textbook. It always works.

Use these rules in order.

The sum of all oxidation numbers of all elements = charge on substance.

		Oxidation Number:	Examples:
1.	Atoms in their elemental state	= 0	Fe, H ₂ , O ₂
2.	Monatomic ions	= charge	F ¹⁻ , Na ¹⁺ , Fe ³⁺

IN COMPOUNDS

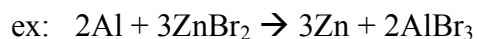
3.	Group 1A	= +1	NaCl, KNO ₃
4.	Group 2A	= +2	MgO
5.	Fluorine	= -1	HF, ClF
6.	Hydrogen	= +1	H ₂ O
7.	Oxygen	= -2	SO ₂ , HClO ₄
8.	Group 7A (Halogen family)	= -1	HCl
9.	Group 6A (Oxygen family)	= -2	PbS ₂

The sum of all oxidation numbers of all elements = charge on substance.

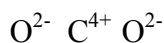
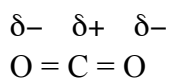
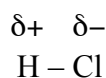
Key: For anything else, (or for a group 7A or group 6A in the presence of higher priority atoms), set its oxidation number = “x”, and solve for “x” such that the ox. #'s = actual charge.

Find Ox #'s for1. H₂OC C:2. PCl₃ P:3. HSO₄⁻ S:4. KMnO₄ Mn:5. Mg₃(PO₄)₂ P:6. HClO₂ Cl:

19.1 Redox Reactions (Review: 5.3)

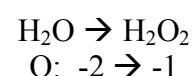
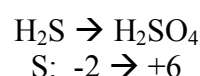
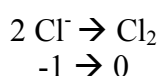
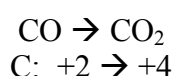
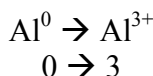
Recognizing Redox Reactions:

- Any reaction in which an elemental substance is involved is always a redox reaction
 - The element can be on either reactant or product side, or both
- Any reaction involving a Change in "oxidation number" is a redox reaction (review 5.4)
 - Oxidation numbers count charges in molecular as well as ionic compounds
 - In a polar covalent bond, a more electronegative atom is given negative charge (credited with bonding electrons), and a less electronegative atom is given positive charge (as if it wasn't seeing the bonding electrons at all)

Notes, Terms

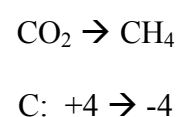
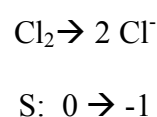
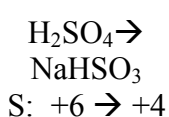
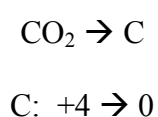
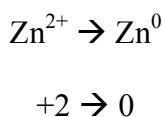
1. Oxidation: loss of e's

- Ox # increases (more positive or less negative)

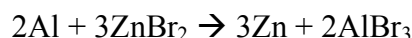


2. Reduction: gain of e's

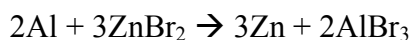
- Ox # is "reduced" (less positive or more negative)



- All redox reactions require both an electron giver (the thing that is oxidized) and an electron taker (the thing that is reduced)
 - Essentially a redox reaction involves a competition for a limited supply of electrons
 - In the example shown, there aren't enough electrons for both Al and Zn to be in their reduced zero-charge form. One or the other must be in its electron-deficient oxidized form



- That Al^{3+} ends up oxidized and Zn^0 ends up reduced suggests that Zn has a higher electron-love than Al
- Competition for limited electrons not unlike acid/base competition for limited H^+ 's

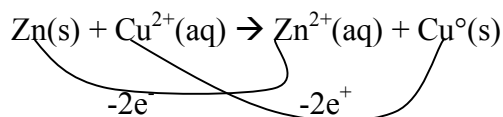


4. "Oxidizing Agent" or "Oxidant": causes something else to be oxidized
 - is itself reduced
 - Zn^{2+} , which is itself reduced, is the "oxidizing agent" because it causes Al to be oxidized
5. "Reducing Agent": causes something else to be reduced
 - is itself oxidized
 - by giving it's electrons to the other guy, it causes the other guy to be reduced, but is oxidized in the process
 - Al, which is itself oxidized, is the "reducing agent" because it causes Zn^{2+} to be reduced
6. "Redox" reduction – oxidation
7. Electrons must balance in a redox reaction: the number given up by the reducing agent must equal the number accepted by the oxidizing agent

Identify the oxidizing and reducing agents and count how many electrons transfer

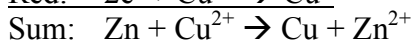
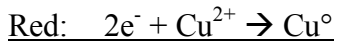
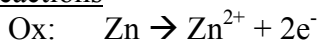
1. $2\text{Na} + 2\text{HCl} \rightarrow 1\text{H}_2 + 2\text{NaCl}$
2. $2\text{KMnO}_4 + 6\text{NaCl} \rightarrow 2\text{MnO}_2 + 3\text{Cl}_2$ (some H_2O , KOH , NaOH also involved)

19.2 Half Reactions, Redox, and Balancing



- both oxidation and reduction must occur
- electrons must balance

Half Reactions



Suppose: Zn^{2+} reacts with Na. Draw the oxidation and reduction half reactions, and balance them for electrons. Combine them to make the sum redox reaction:

Reduction

Oxidation

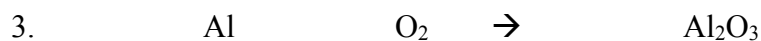
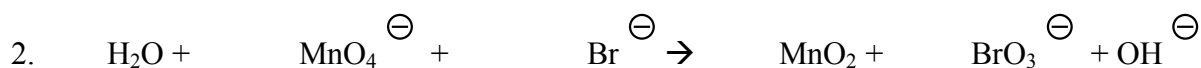
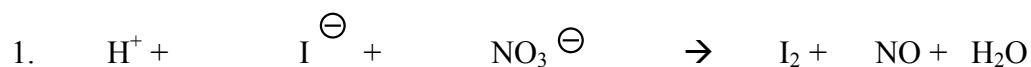
Net Sum

Balancing Redox

1. Identify oxidation numbers for redox actors
2. Set coefficients for them so that the **#e's released = #e's accepted**
 - focus completely on the atoms whose oxidation numbers change
3. Then balance any redox spectators
4. Check at the end to make sure:
 - Charges balance
 - Atoms balance

Note: Test problems will give you all of the species involved. Some OWL problems will be harder and will not include all of the chemicals

Balance (Test Level)

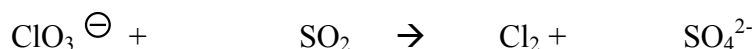


Some Harder OWL-Level problems:

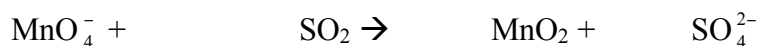
- Sometimes H_2O , OH^- , H^+ are omitted, and need to be added in order to balance oxygens and hydrogens
- In knowing how to do this, it is helpful to distinguish acid versus base conditions
- Under acid conditions, it's appropriate to have H^+ but not OH^-
- Under base conditions, it's appropriate to have OH^- but not H^+

Acid Conditions	Base Conditions
<ol style="list-style-type: none"> Identify oxidation numbers for redox actors Set coefficients for them so that the #e's released = #e's accepted <ul style="list-style-type: none"> focus completely on the atoms whose oxidation numbers change Add H_2O's to balance oxygen Add H_2O's as needed to balance <u>oxygens</u> Add H^+'s as needed to balance <u>hydrogens</u> and charge Check at the end to make sure: <ol style="list-style-type: none"> Charges balance Atoms balance 	<ol style="list-style-type: none"> Identify oxidation numbers for redox actors Set coefficients for them so that the #e's released = #e's accepted <ul style="list-style-type: none"> focus completely on the atoms whose oxidation numbers change Add OH^-'s to balance charge Add OH^-'s as needed to balance <u>charge</u> Add H_2O's to balance hydrogens Check at the end to make sure: <ol style="list-style-type: none"> Charges balance Atoms balance

- 1. **Acid** conditions:



- 2. **Base** conditions:



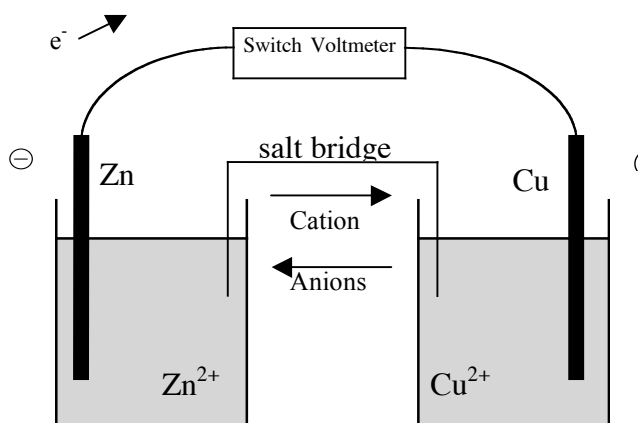
19.3 Electrochemical Cells



- when redox partners are in direct contact (in the same beaker, in the same solution) direct electron transfer occurs: no measurable or useful electron flow

Electrochemical (“Voltaic”) Cell: redox reactants are separated, so electron flow is forced to go through external circuit \Rightarrow measurable, useful electricity

Setup (fig 19.5 Moore, Brown 20.5)



2 Solid metals = “electrodes”

- electrodes can be metal, plates or wires, or graphite or some other materials: (must be conductive)
- “Anode” = electrode Oxidized (vowels) $\text{Zn} \rightarrow \text{Zn}^{2+}$
 - electron source
 - dissolving
 - negative sign on a battery
- “Cathode” = electrode reduced (consonant) $\text{Cu}^{2+} \rightarrow \text{Cu}$
 - e- receiver
 - physically electrode grows (Cu^0 forming)
 - positive sign on battery

Two “Half Cells” and “Half Reactions”

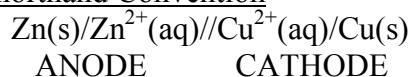
- “Anode” side = Where the oxidation half reaction occurs ($\text{Zn} \rightarrow \text{Zn}^{2+}$ beaker)
- “Cathode” side = Where the reduction half reaction occurs ($\text{Cu}^{2+} \rightarrow \text{Cu}$ beaker)

Salt Bridge Connector or Semipermeable Membrane

- In an electrochemical cell, cations are being produced in the anode half ($\text{Zn} \rightarrow \text{Zn}^{2+}$), and cations are being removed in the reduction side ($\text{Cu}^{2+} \rightarrow \text{Cu}$)
- Solutions need to maintain charge balance, so the anode side needs to either gain anions or lose excess cations, and the cathode side needs to either gain cations or lose anions in order to charge-balance.
- This is accomplished via either a “salt bridge” or “semipermeable membrane” (“porous barrier”): something that allows ions to pass

Direction of Ion flow:

- Cations move from anode (being produced) to cathode (to replace cations reduced)
- Anions move from cathode to anode, to balance forming cations

Cell Shorthand Convention

// = barrier between half cells

/ = distinction between electrodes and ions

Many variations on electrochemical cell engineering

- Special cells when H₂ gas is produced (Brown 20.8)
- Many types with conductive graphite electrodes on which surface other redox half-reactions occur
- “Dry cells” involving thick paste mixtures rather than any solvent (many batteries)

19.4 Electrochemical Cells and Voltage

- Voltage depends on redox reactivity, the chemical force for electron transfer

E_{cell} = cell potential in volts ($V = J/C$ $C = \text{coulomb of electricity}$)

E°_{cell} = **standard** potential

Standard Conditions

- 1.0 M concentration
- 25°C
- gases (if any) at 1.0 atm

Since a cell consists of 2 half cells:

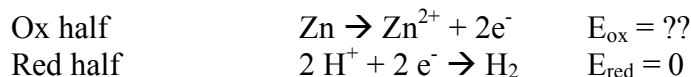
$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidation}} + E^{\circ}_{\text{reduction}}$ <p style="text-align: center;">Anode Cathode</p>

Each half reaction has an E° , relative to self-defined **reference half reaction**



Show Table 19.1, OWL Handout

Example: $\text{Zn} + 2\text{HCl} \rightarrow \text{H}_2 + \text{ZnCl}_2$ $E_{\text{cell}}^{\circ} = +0.76$



$$E^{\circ}_{\text{cell}} = +.76 = E_{\text{ox}} + E_{\text{red}} = E_{\text{ox}} + 0 \quad \text{so } \boxed{E^{\circ}_{\text{ox}} = +0.76 \text{ V}}$$

The same approach can be used to find the potentials for any other half reaction.

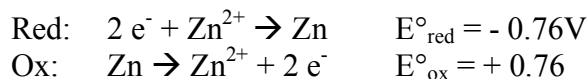
19.5 Using E°_{cell} and known Half Potentials

$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}}$$

1. Tables list reduction halves E°_{red}

$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	+0.77V
$\text{Cu}^{2+} \rightarrow \text{Cu}$	+0.34V
$2 \text{H}^+ \rightarrow \text{H}_2$	0.00
$\text{Pb}^{2+} \rightarrow \text{Pb}$	-0.13
$\text{Ni}^{2+} \rightarrow \text{Ni}$	-0.25
$\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$	-0.74

2. When a half is reversed, sign reverses



$$E^\circ_{\text{ox}} = -E^\circ_{\text{red}}$$

Q: What is the oxidation potential for $\text{Cu} \rightarrow \text{Cu}^{2+}$?

3. Key skill: Given known halves, deduce E°_{cell} .



4. Stoichiometry coefficients don't matter to E° 's

- In previous example, the reduction potential for Fe^{3+} was still +0.77 V, even though the balanced reaction had 2 Fe^{3+} ions being reduced.

5. Key skill: Given an overall E°_{cell} and one known or knowable half potential, calculate the half potentials for the other half.



Find E°_{red} for: $\text{Sn}^{2+} \rightarrow \text{Sn}$

Find E°_{ox} for: $\text{Sn} \rightarrow \text{Sn}^{2+}$

6. All redox half-reaction potentials are relative to H^+ reduction ($E^\circ_{\text{red}}=0$) or H_2 oxidation ($E^\circ_{\text{ox}}=0$)

$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	+0.77V
$\text{Cu}^{2+} \rightarrow \text{Cu}$	+0.34V
$2 \text{H}^+ \rightarrow \text{H}_2$	0.00
$\text{Pb}^{2+} \rightarrow \text{Pb}$	-0.13
$\text{Ni}^{2+} \rightarrow \text{Ni}$	-0.25
$\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$	-0.74

7. For a product-favored reaction, $E^\circ_{\text{cell}} = \text{positive}$
- more positive the better

Q: Which of the following are favorable redox reactions?

- a. $\text{Cu} + \text{Sn}^{2+} \rightarrow \text{Sn} + \text{Cu}^{2+}$ $E^\circ_{\text{cell}} = -0.48\text{V}$
- b. $\text{Cu} + 2\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 2\text{Fe}^{2+}$ $E^\circ_{\text{cell}} =$
- c. $\text{Cu}^{2+} + \text{Ni} \rightarrow \text{Ni}^{2+} + \text{Cu}$ $E^\circ_{\text{cell}} =$

Logic:

8. For half reactions, the more positive the more favorable

<u>Reductions</u>			<u>Oxidations</u>		
$\text{F}_2 \rightarrow 2 \text{F}^-$	+2.87	great	$2 \text{F}^- \rightarrow \text{F}_2$	-2.87	terrible
$\text{Cu}^{2+} \rightarrow \text{Cu}$	+0.34	good	$\text{Cu} \rightarrow \text{Cu}^{2+}$	-0.34	bad
$\text{Ni}^{2+} \rightarrow \text{Ni}$	-0.25	bad	$\text{Ni} \rightarrow \text{Ni}^{2+}$	+0.25	good
$\text{Li}^+ \rightarrow \text{Li}$	-3.0	terrible	$\text{Li} \rightarrow \text{Li}^+$	+3.0	great

9. Chemical Logic: Redox patterns depend on electron love (predictable periodic trends)
- Higher love for electrons \rightarrow more favorable to be reduced (gain electrons)
 - Higher love for electrons \rightarrow more unfavorable to be oxidized (lose electrons)
 - Fluorine is the most electronegative of the four elements, lithium the least
 - Fluorine loves to be reduced (gain electrons), so has best reduction potential
 - Fluoride hates to be oxidized (lose electrons), so has the worst oxidation potential
 - Lithium has low electron love, so is easily oxidized
 - Because it is so unattractive towards electrons, lithium cation has lousy oxidation potential

Q1: Based on table, rank the electron affinities for Cu, H₂, Ni, and Pb

Q2: Which would be a stronger oxidizing agent (stealer of e's), Cu²⁺ or Ni²⁺ ?

Q3: Which would be a stronger reducing agent (giver of e's), Cu or Ni ?

Redox conjugates: Oxidizing vs. Reducing Agents, Oxidized versus Reduced Forms

Love For Electrons	Strength as Oxidizing Agents		Strength as Reducing Agents	Love For Electrons
		Fe ³⁺ → Fe ²⁺	+0.77V	
		Cu ²⁺ → Cu	+0.34V	
		2 H ⁺ → H ₂	0.00	
		Pb ²⁺ → Pb	-0.13	
		Ni ²⁺ → Ni	-0.25	
		Cr ³⁺ → Cr ²⁺	-0.74	

On table:

Left Side

- 1 **Oxidized form** (less electrons)
- 2 **Oxidizing Agents** (may wish to grab electrons from something else and so oxidize the other thing)
- 3 Higher up = stronger oxidizing agent
- 4 Higher up = greater love for electrons
- 5 Higher E°_{red} ⇒
 - a. more easily reduced
 - b. stronger love for e⁻'s
 - c. stronger oxidizing agent

Right Side

- Reduced Form** (more electrons)
Reducing Agents (able to give electrons to something else and so reduce the other thing)
 Lower down = stronger reducing agent
 Lower down = lesser love for electrons

- Often things aren't charted like this. But for two things in their oxidized forms, the one with the higher E°_{red} ⇒
 - a. more easily reduced
 - b. stronger love for e⁻'s
 - c. stronger oxidizing agent

If charting reduction potentials:

- upper left = strongest oxidizing agent = max electron love = most easily reduced
- bottom right = strongest reducing agent = minimum electron love = most easily oxidized.

Some Representative Problem Types

- a. Rank the oxidizing agents by strength
- b. Rank the reducing agents by strength
- c. Which will react with Cu²⁺?
- d. Which will react with Cu⁰?

Brown Fig. 20.10

Love For Electrons	Strength as Oxidizing Agents		Strength as Reducing Agents	Love For Electrons
		$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	+0.77V	
		$\text{Cu}^{2+} \rightarrow \text{Cu}$	+0.34V	
		$2 \text{H}^+ \rightarrow \text{H}_2$	0.00	
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		$\text{Ni}^{2+} \rightarrow \text{Ni}$	-0.25	
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- Strongest Oxidizing agent: top left (max e- love)
- Strongest Reducing agent: bottom right (min e- love)

Odds and Ends

- An oxidizing agent on table will react (product-favored) with any reducing agent lower
 - Will not react with any reducing agent higher (reactant favored)
 - A reducing agent will only react with an oxidizing agent higher on the chart
 - What species would react with Pb^{2+} ?
 - What species would react with Pb?
- For two species to react, one must be in reduced form (reducing agent), and the other in oxidized form (oxidizing agent)
 - What of the following species could react with Cu^{2+} ?

$2 \text{H}^+ \quad \text{H}_2 \quad \quad \quad \text{Pb}^{2+} \quad \text{Pb} \quad \quad \quad \text{Ni} \quad \text{Ni}^{2+} \quad \quad \quad \text{Cr}^{2+} \quad \text{Cr}^{3+}$
 - What of the following species could react with Cr^{2+} ?

$2 \text{H}^+ \quad \text{H}_2 \quad \quad \quad \text{Pb}^{2+} \quad \text{Pb} \quad \quad \quad \text{Ni} \quad \text{Ni}^{2+}$
- Given redox chart, rank electron love and basically predict which reactions are or aren't favorable
- Based on periodic table, predict reactivity **without redox table** (based on general periodic patterns in electron love)
 - General Activity as Reducing Agents (increasing e- love)

$\text{G1} > \text{G2} > \text{Al} > \text{most T-metals} > \text{H}_2 > \text{coinage metals}$
(active metals)

Ex. Li Mg Al Zn, Fe, Cr H₂ Cu, Au

$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	+0.77V
$\text{Cu}^{2+} \rightarrow \text{Cu}$	+0.34V
$2 \text{H}^+ \rightarrow \text{H}_2$	0.00
$\text{Pb}^{2+} \rightarrow \text{Pb}$	-0.13
$\text{Ni}^{2+} \rightarrow \text{Ni}$	-0.25
$\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$	-0.74

5. Given 2 reduction potentials, figure out how a product-favored cell would be constructed and calculate the standard voltage
- Keep the more favorable reduction potential as the reduction half, but reverse the other into its oxidation version
 - Then sum $E^\circ_{\text{red}} + E^\circ_{\text{ox}}$ to get E°_{cell}

Examples

e. Determine what the voltage would be for a cell consisting of Pb^{2+}/Pb and Ni^{2+}/Ni .

f. Determine what the voltage would be for a cell consisting of Pb^{2+}/Pb and Cu^{2+}/Cu .

6. Use observed reactivities to determine:
- relative love for electrons
 - relative strength as reducing agents
 - relative strength as oxidizing agents
 - relative redox table (“activity series”)

Example: $\text{X} + \text{Y}^{2+} \rightarrow \text{Y} + \text{X}^{2+}$ Product-favored redox. Questions: Between X and Y:

- Which element loves electrons more?
- What thing is the strongest reducing agent?
- Which thing is the strongest oxidizing agent?
- Draw a little reduction potential chart, with the strongest oxidizing agent in the upper left corner as usual

A Redox Reaction Always favors “weaker” side

Example: $Q + P^{2+} \leftarrow P + Q^{2+}$ Reactant-favored redox. Between P and Q:

- Which element loves electrons more?
- What thing is the strongest reducing agent?
- Which thing is the strongest oxidizing agent?
- Draw a little reduction potential chart, with the strongest oxidizing agent in the upper left corner as usual

A Redox Reaction Always favors “weaker” side

Miscellaneous Problems

- $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$ $E^\circ = 0.32V$
 What is the “reduction potential” for $Fe^{2+} (Fe^{2+} \rightarrow Fe^\circ)$ given the above potential, and given that $Zn^{2+} \rightarrow Zn$ $E^\circ_{red} = -0.76$

- Find E° for product favored reaction involving the following, and balance the reaction

$Fe^{3+} \rightarrow Fe^{2+}$	0.77
$Cu^{2+} \rightarrow Cu$	0.34

 - keep more favorable one as reduction
 - reverse less favorable to make it an oxidation
 - sum E°_{ox} and E°_{red}
 - adjust coefficients to balance e^- 's

- Ditto for

$Br_2 \rightarrow 2 Br^-$	$+1.06$
$Zn^{2+} \rightarrow Zn$	-0.76

	V
$\text{Ag}^+ \rightarrow \text{Ag}$	+0.80
$\text{Cu}^{2+} \rightarrow \text{Cu}$	+0.34
$\text{Zn}^{2+} \rightarrow \text{Zn}$	-0.76
$\text{Al}^{3+} \rightarrow \text{Al}$	-1.66
$\text{Mg}^{2+} \rightarrow \text{Mg}$	-2.36

12. Which species react with Cu^{2+} ?

13. Which species react with Zn^0 ?

14. Which element loves e's the most? Least?

15. $\text{NiCl}_2 + \text{H}_2 \rightarrow \text{Ni} + 2 \text{HCl}$ $E^\circ = -0.28 \text{ V}$

a. Product favored or not?

b. Is reduction potential for Ni^{2+} positive?

19.6 E°_{cell} and ΔG° , E° and K

	ΔG	E°_{cell}	K
Product Favored	neg	pos	large
Reactant Favored	pos	neg	small
**Equilibrium	0	0	1

ΔG° and E°_{cell} have opposite signs, but are related

- both provide measurements for the favorability or unfavorability of a reaction
- obviously E°_{cell} is more limited, to redox reactions
- K is also related, since it too relates to how favorable or unfavorable a reaction is
- ΔG° = "free energy" available to do be released and do work
- E°_{cell} also reflects the amount of energy that is released to do work when a favorable redox transfer occurs
 - The "free energy" in a cell is really the free energy to do the work of moving electrons and to the work that flowing electricity can do

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -96.5nE^\circ_{\text{cell}}$$

n = number of electrons transferred in the balanced equation (now coefficients matter!!)

- crucial that you have a correctly balanced redox reaction, and can count how many electrons transfer

F = Faraday's constant = **96.5** to get ΔG in kJ/mol

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} \qquad \Delta G^\circ = -96.5nE^\circ_{\text{cell}}$$

Units	$F = \frac{96,500\text{C}}{\text{mole } e^-}$	$V = \frac{\text{J}}{\text{C}} \text{ so } C = \frac{\text{J}}{\text{V}}$	C = coulomb, unit of electricity, amount of charge
Substituting	$F = \frac{96,500\text{J}}{\text{mole } e^- \cdot \text{V}}$	$F = \frac{96.5 \text{ kJ}}{\text{mole } e^- \cdot \text{V}}$	Thus when "n" is moles of electrons, and E°_{cell} is in volts, the units cancel and only kJ are left.

Electrochemistry-Related Units/Terms: For interest, not for test

C = Coulomb = quantity of electrical charge = $6.24 \cdot 10^{18}$ electrons

- 1 mole of electrons = 96,500 C

A = amp = rate of charge flow per time = Coulombs/second

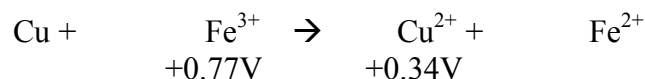
V = volt = electrical power/force/strength; difference in electrical potential energy = J/C

- Force for moving electrons and charge
- Not all Coulombs of charge have the same energy/power/force/ability to do work
- Just like dropping a brick from one cm has less force than dropping it from two meters high

F = Faraday = charge per chemical amount (the mole) = $\frac{96,500\text{C}}{\text{mole } e^-} = \frac{96.5 \text{ kJ}}{\text{mole } e^- \cdot \text{V}}$

Watt = amount of energy

1. Balance the reaction, and find ΔG° given the reduction potentials shown



2. $\text{Zn} + \text{Cr}^{3+} \rightarrow \text{Zn}^{2+} + \text{Cr} \quad \Delta G^\circ = -11.6 \text{ kJ/mol}$

a. Balance the reaction, and calculate E°_{cell} .

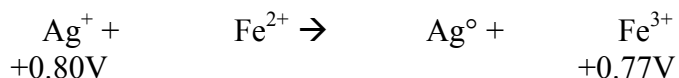
b. If the reduction potential for Zn^{2+} is -0.76V , what is the reduction potential for Cr^{3+} ?

Cell Voltage and K Likewise voltage and K linked!!

- The more favorable and positive E°_{cell} , the larger and more favorable is K
- Again, “n” = number of electrons transferred, so you need balanced reaction
- Caution: K values often work out to be enormous (calculator problems)

$$\log K = nE^\circ_{\text{cell}} / (0.0592)$$

3. Calculate K, given reduction potentials.



19.7 The Effect of Concentration on Cell Potential: Voltages when Concentrations are not all Equal to Standard 1.0 M

1. E° assumes 1.0 M concentrations for any soluble species (and 1.0 atm pressure for any gas)
 - rarely actually true!
2. For any real reaction, concentrations change as the reaction proceeds
 - As the concentrations change, the voltage drops
 - Actual voltage continues to drop until the battery is dead = 0V = equilibrium
 - At equilibrium, $E_{\text{actual}} = 0 \text{ V}$

$$\text{Nernst Equation: } E_{\text{actual}} = E^\circ - \frac{.0592}{n} \log Q$$

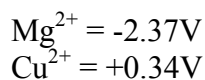
n = number of e⁻s transferred (need balanced equation, coefficients)

Q = ratio of actual concentrations (K format, but using actual concentrations)

- Recall: solids, liquids don't appear in K or Q, only aqueous solutes or gases

Problems

1. Calculate actual voltage for Mg/Mg²⁺(0.10M)//Cu²⁺(0.001M)/Cu given the following reduction potentials:



Logic Steps

Nernst Equation:	$E_{\text{actual}} = E^{\circ} - \frac{.0592}{n} \log Q$
------------------	--

2. Calculate actual voltage for Cu/Cu²⁺(1.0M)//Ag⁺(0.032M)/Ag

$$\begin{array}{l} E_{\text{red}}^{\circ} \\ \text{Ag}^+ \quad +0.80\text{V} \\ \text{Cu}^{2+} \quad +0.34\text{V} \end{array}$$

3. $2 \text{Ag}^+(\text{aq}) + \text{Zn}(\text{s}) \rightarrow 2 \text{Ag}(\text{s}) + \text{Zn}^{2+}(\text{aq})$

$$E_{\text{red}}^{\circ} \quad +0.80 \qquad \qquad \qquad -0.76$$

If a cell with $[\text{Ag}^+] = 0.20 \text{ M}$ has $E_{\text{actual}} = 1.63\text{V}$, what is $[\text{Zn}^{2+}]$

Cell Potential and Equilibrium

At equilibrium:

- $E_{\text{actual}} = 0 \text{ V}$
- $Q=K$

$$\text{So, at equilibrium } 0 = E^{\circ} - \frac{.0592}{n} \log K$$

$$\text{At equilibrium: } \boxed{E^{\circ} = \frac{.0592}{n} \log K}$$

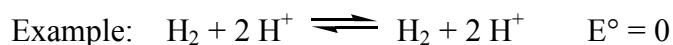
Finding E° given K

$$\text{Rearranged: } \boxed{\log K = nE^{\circ}_{\text{cell}} / (.0592)}$$

Finding K given E°_{cell}

“Concentration cells”: anode and cathode use the same things, but with ions at different concentrations

- at equilibrium, the concentrations would be equal, so the voltage drive is to equalize



$$\text{So } E_{\text{actual}} = (-0.592/n) \log Q$$

This kind of voltage is key to pH meters, neurons (19.8)

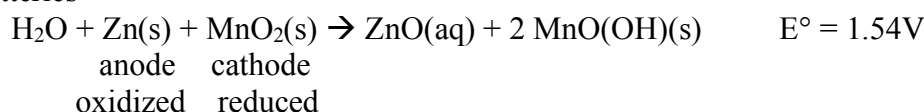
- pH meter: dip meter with known $[\text{H}^+]$ into a solution, measured voltage reflects solution $[\text{H}^+]$
- neurons: The H^+ concentration differs inside and outside cell membranes. This creates a voltage which is the key for nerve sensation

19.9 Common Batteries

A. Primary (“Dry Cell”): Nonrechargeable

- run till concentration achieves equilibrium = dead = toss

1. Alkaline batteries



- reduction occurs at a graphite electrode
- this is common when an electrode doesn't involve a redox
- flashlights, radio, toys, Jasperse insulin pump, Jasperse blood testers, tooth brush, etc.

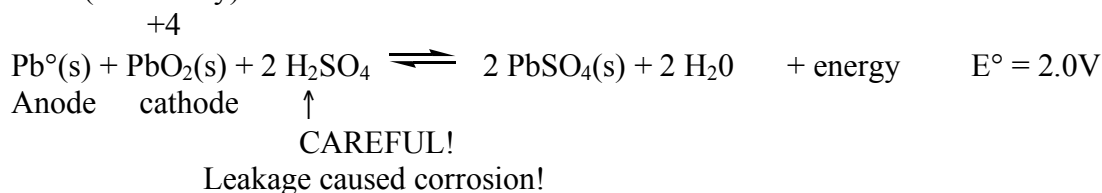
2. Mercury battery



- Less power than alkaline batteries, but mercury batteries are physically smaller
- used in small things (calculators, watches, cameras,...)
- mercury is poisonous, so battery disposal an environmental issue

B Secondary Batteries (“nicad” and “car”) = Rechargeable

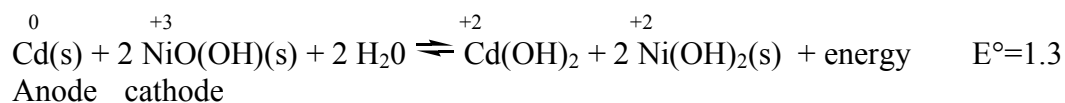
1. Lead-acid (car battery)



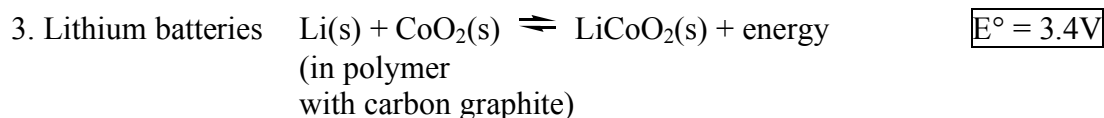
- The $\text{PbSO}_4(\text{s})$ coats electrodes, so reaction can be reversed when “recharged”
- Each cell is 2.0V: six alternating cathode/anodes in series sums to 12V
- Energy during a recharge drives it in the reverse direction, to the left
- Side products during recharge
 - Ox: $6 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}_3\text{O}^+ + 4\text{e}^-$
 - Red: $4 \text{H}_2\text{O} + 4\text{e}^- \rightarrow 2 \text{H}_2 + 4 \text{OH}^-$
- Side Both H_2 and O_2 are produced during the recharge. These are a perfect recipe for an explosion. Why no sparks or cigarette lighting is allowed around a car battery

2. NiCad $E^\circ=1.3$

- electric shavers, dustbusters, video camcorders, rechargeable power toothbrush, any rechargeable cordless appliances



- again, solid products stay on electrodes, so the reaction can reverse upon treatment with electrical energy

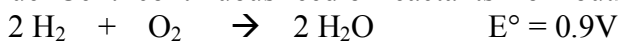
Pros:

- Big voltage \rightarrow good for fueling energy eaters, like laptops, cameras, cell phones
- Light weight

Cons

- More expensive

19.10 Fuel Cell: continuous feed of reactants from outside to electrodes (interest, not test)



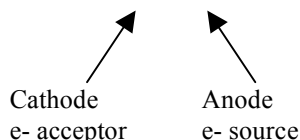
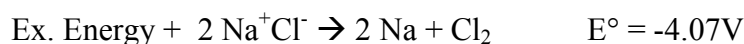
Anode cathode

- $\text{H}_2 + \text{O}_2$ light, so good fuels, high energy efficiency
- Spaceships: 500 pounds of fuel enough energy for 11 days
- Dream: come up with some way to use solar/wind energy to produce H_2 from water, then use the H_2/O_2 fuel cell to get energy and regenerate H_2O , pollution free
- Fuel cells future for cars??

19.11 Electrolysis: Using outside electrolysis to force unfavorable redox reactions to proceed to product side

- key route to elements not found in nature: metals, H_2 , Cl_2 ,...

A. Electrolysis of Molten Salts (“molten” = melted, pure liquid salts in absence of solvent, super hot!!)

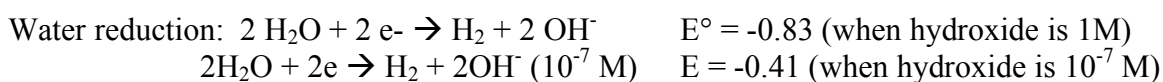


(Brown, Gillespie overheads)

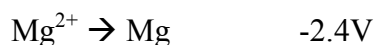
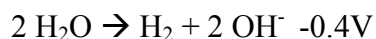
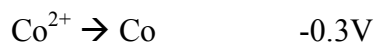
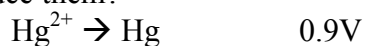
- products must be kept separate so can't react

B. Electrolysis of salts in Water: Can only process ions that are more reactive than water

- At each electrode, the most reactive candidate reacts
 - In water, water competes at both the cathode (reduction) and anode (oxidation)
- Reduction/Cathode
 - If a cation is harder to reduce than water itself, water will just get reduced instead
 - If you want to reduce something that is harder to reduce than water, you need to do it as a molten salt rather than in water
 - Only cations with reduction potentials more positive than -0.83 V (in basic water) or -0.41 V (in neutral water) can be reduced in water.
 - Water's reduction potential is pH dependent (since hydroxide concentration factors)



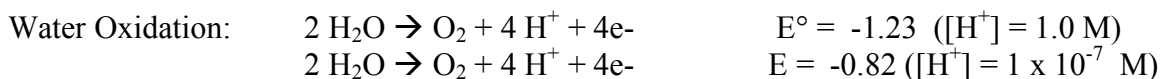
Problem: Which of the following metal cations could be converted into elemental metal by electrolysis in water? For which metal cations would you need to use molten salt if you wanted to reduce them?



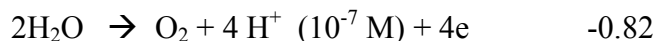
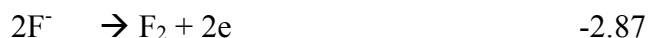
- Easily reduced cations (Zn^{2+} , Ni^{2+} , Cr^{3+} , Sn^{2+} , etc.) can be reduced to elemental form in water.
- Cations of Active metals can't (K^+ , Mg^{2+} , Na^+ , ...). If they are to be reduced to elemental form, they must be reduced as molten salts.

Oxidation/Anode

- If a reduced species is harder to oxidize than water itself, water will just get oxidized instead
- If you want to oxidize something that is harder to oxidize than water, you need to do it as a molten salt rather than in water
- Only reduced species with oxidation potentials more positive than -1.23 V (in acidic water) or -0.82 (in neutral water) can be oxidized in water.



Problem: Which of the following oxidations could be conducted by electrolysis in water? And which processes would require molten salts??





1. Given the reduction potentials, what is the product at the anode and at the cathode when a current is passed through an aqueous solution of SnCl_2 ? (Hint: remember which chemicals and ions are really in the solution and subject to the electrolysis.)

Anode

- Sn
- Cl_2
- O_2
- H_2
- none of the above

Cathode

- Sn
- Cl_2
- O_2
- H_2
- none of the above

2. Given the reduction potentials, what is the product at the anode and at the cathode when a current is passed through an aqueous solution of MnI_2 ? (Hint: remember which chemicals and ions are really in the solution and subject to the electrolysis.)

Anode

- Mn
- I_2
- O_2
- H_2
- none of the above

Cathode

- Mn
- I_2
- O_2
- H_2
- none of the above

Electroplating: metal cation \rightarrow elemental metal (reduction at cathode)

- metal forms on surface of cathode
- many metals are “plated” on outside of things in their way
- “Silverware” for a long time involved plating a coating of silver over something else
- Art objects, etc.
- Materials that are otherwise subject to rust, corruptions are often electroplated with a coating that is resistant to air, rain, and acid.

Some Famous Electrolyses (trivia):

- NaCl in H_2O \rightarrow NaOH (anode) and HCl and O_2 (cathode) production NaOH , HCl
- NaCl (molten) \rightarrow Na metal (cathode) + Cl_2 (anode) Cl_2 production

19.12 Electrolysis Calculations

- **1 mol electrons = 96,500 C (Coulombs)**

current, time, and moles of electrons are related

$$A \text{ (amp)} = C/\text{sec}$$

A Derivation and 3 Permutations of an equation:

$$\text{Moles electrons} = \frac{\text{current}(A) \cdot \text{sec}}{96,500}$$

$$\text{Sec} = \frac{(\text{moles})96,500}{A}$$

$$A = \frac{(\text{moles})96,500}{\text{sec}}$$

Finding moles, given
current and time

Finding time, given
moles and current

Finding current, given
moles and time

Qualitative Relationship (and vice versa):

Amps + time → **moles of electrons** → **moles of substance redoxed** → **grams of substance**

Keys:

1. Grams of substance and moles of substance are interconverted by molecular weight
2. Be sure to factor how many moles of electron are involved per moles of chemical formula

1. How many grams of Al (27g/mol) is produced in 1.0 hour by electrolysis of AlCl_3 at 10.0A current?

2. At 3.2A, how long will it take to make 10g of Zn (65.4 g/mol) from ZnBr_2 ?

3. What current in amps is required to make 10 grams of Cl_2 (71 g/mol) from AlCl_3 in one hour?

19.13 Corrosion

Corrosion involves a product-favored oxidation of a metal exposed to environment (O_2 , H^+ , H_2O ,...)

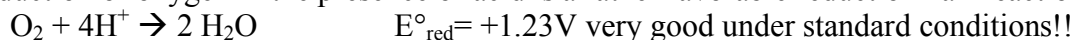
The metal being oxidized always functions as the oxidation half

Molecular oxygen is reduced to water in the presence of acid as the reduction half

As for any favorable redox reaction, the sum of the two half reactions must give positive E

Thus, the favorability of the oxygen reduction half is critical in determining which metals can and cannot be oxidized

The reduction of oxygen in the presence of acid is a rather favorable reduction half reaction



Obviously acid that is “standard conditions” 1.0 M is rare

The more acidic the water environment, the more favorable oxygen reduction is and the more metals can be corroded

Under 1.0 M acid conditions ($pH = 1$), any metal that has an oxidation potential better than -1.23 V can be oxidized in air

Under neutral $pH = 7$ conditions, any metal that has an oxidation potential better than -0.82V can be oxidized in air

Most metals are included, especially under acidic conditions!!

Why most metals are not found in their elemental form in nature, but rather as ions

Exception: gold!!

Metals usually end as metal oxides or sometimes metal hydroxides

Ag tarnish

Cu “greening”

Fe rusting

Rust: $2 Fe + O_2 + 2 H_2O \rightarrow 2 Fe(OH)_2 \rightarrow \rightarrow \rightarrow Fe_2O_3$ red-brown rust

Practical notes:

- Corrosion often speeded by H^+ and/or ionic salts that acidity water
- Gold has always been valued because unlike other oxidizable metals, it retains it's elemental form and it's lustrous golden elemental surface appearance.
- Most metals get coated with a film of hard metal oxide, which ends up protecting the interior or the metal.
 - The interior stays elemental metal, but is protected by sheath of hard metal oxide from exposure to air.
 - Sometimes it takes chemical activation to clear the oxide film and enable the elemental metal inside to be exposed for chemical reactions.
- Why does iron have such a special rusting problem?
 - Iron is bad because iron oxide (rust) forms flakes that break off.
 - As a result, the interior iron is **not** protected and is continuously exposed for further corrosion.

Prevention

- Coat iron surface with something that resists corrosion and protects.

Development of improved and more resistant sealants has been a major priority of auto-industry

- “Galvanized iron”-Iron materials are electroplated with Zn, which is more easily oxidized than iron but oxidizes to give a hard, protective $Zn(OH)_2$ coating.

Chapter 19 Electrochemistry Math Summary

Relating Standard Cell Potential to Standard Half Cell Potentials

$$E^\circ_{\text{cell}} = E^\circ_{\text{oxidation}} + E^\circ_{\text{reduction}} \quad (\text{standard conditions assume } 1.0 \text{ M concentrations})$$

Relating Half Cell Potentials when Written in Opposite Directions

$$E^\circ_{\text{ox}} = -E^\circ_{\text{red}} \quad \text{for half reactions written in opposite directions}$$

Relating Standard Cell Potentials to ΔG

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} \quad (\text{to give answer in kJ, use } F = 96.485)$$

$$F = 96,500 \text{ C/mol}$$

n = number of electrons transferred

Relating Actual Cell Potential to Standard Cell Potential when Concentrations aren't 1.0-M

$$E_{\text{cell}} = E^\circ_{\text{cell}} - [0.0592/n] \log Q \quad (Q = \text{ratio of actual concentrations})$$

Relating Standard Cell Potential to Equilibrium Constant

$$\log K = nE^\circ/0.0592$$

Relating Actual Cell Potential to Actual Concentrations in Concentration Cells

$$E_{\text{cell}} = -[0.0592/n] \log Q \quad \text{for concentration cells, where anode and cathode differ only in concentration, but otherwise have same ions}$$

Relating # of Moles of Electrons Transferred as a Function of Time and Current in Electrolysis

$$1 \text{ mol } e^- = 96,500 \text{ C}$$

$$\text{moles of electrons} = [\text{current (A)} \cdot \text{time (sec)}] / 96,500 \quad \text{for electrolysis, moles, current, and time are related.}$$

$$\text{rearranged: time (sec)} = (\text{moles of electrons})(96500) / \text{current (in A)}$$

Note: 3600 sec/hour

$$\text{so time (hours)} = (\text{moles of electrons})(26.8) / \text{current (in A)}$$

Electrochemistry-Related Units

C = Coulomb = quantity of electrical charge = $6.24 \cdot 10^{18}$ electrons

• 1 mole of electrons = 96,500 C

A = amp = rate of charge flow per time = C/sec

V = volt = electrical power/force/strength = J/C

$$F = \text{Faraday} = \frac{96,500 \text{ C}}{\text{mole } e^-} = \frac{96.5 \text{ kJ}}{\text{mole } e^- \cdot \text{V}}$$

Assigning Oxidation Numbers (See Section 5.4)

This is a more complete set of rules than your textbook. It always works.

Use these rules in order.

The sum of all oxidation numbers of all elements = charge on substance.

		Oxidation Number:	Examples:
1.	Atoms in their elemental state	= 0	Fe, H ₂ , O ₂
2.	Monatomic ions	= charge	F ¹⁻ , Na ¹⁺ , Fe ³⁺

IN COMPOUNDS

3.	Group 1A	= +1	NaCl, KNO ₃
4.	Group 2A	= +2	MgO
5.	Fluorine	= -1	HF, ClF
6.	Hydrogen	= +1	H ₂ O
7.	Oxygen	= -2	SO ₂ , HClO ₄
8.	Group 7A (Halogen family)	= -1	HCl
9.	Group 6A (Oxygen family)	= -2	PbS ₂

The sum of all oxidation numbers of all elements = charge on substance.

Key: For anything else, (or for a group 7A or group 6A in the presence of higher priority atoms), set its oxidation number = "x", and solve for "x" such that the ox. #'s = actual charge.

Find Ox #'s for

1. H ₂ OC C:	2. PCl ₃ P:
3. HSO ₄ ⁻ S:	4. KMnO ₄ Mn:
5. Mg ₃ (PO ₄) ₂ P:	6. HClO ₂ Cl:

Balancing Redox: Simple Cases where all Reactants and Products are Provided

1. Identify oxidation numbers for redox actors
2. Set coefficients for them so that the **#e's released = #e's accepted**
 - focus completely on the atoms whose oxidation numbers change
3. Then balance any redox spectators
4. Check at the end to make sure:
 - Charges balance
 - Atoms balance

Note: Test problems will give you all of the species involved. Some OWL problems will be harder and will not include all of the chemicals

Some Harder OWL-Level Redox-Balancing Problems: When some necessary chemicals are omitted

- a. Sometimes H_2O , OH^- , H^+ are omitted, and need to be added in order to balance oxygens and hydrogens
- b. In knowing how to do this, it is helpful to distinguish acid versus base conditions
- c. Under acid conditions, it's appropriate to have H^+ but not OH^-
- d. Under base conditions, it's appropriate to have OH^- but not H^+

<u>Acid Conditions</u>	<u>Base Conditions</u>
<ol style="list-style-type: none"> 1. Identify oxidation numbers for redox actors 2. Set coefficients for them so that the #e's released = #e's accepted <ul style="list-style-type: none"> • focus completely on the atoms whose oxidation numbers change Add H_2O's to balance oxygen 3. Add H_2O's as needed to balance <u>oxygens</u> 4. Add H^+'s as needed to balance <u>hydrogens</u> and charge 5. Check at the end to make sure: <ol style="list-style-type: none"> a. Charges balance b. Atoms balance 	<ol style="list-style-type: none"> 1. Identify oxidation numbers for redox actors 2. Set coefficients for them so that the #e's released = #e's accepted <ul style="list-style-type: none"> • focus completely on the atoms whose oxidation numbers change Add OH^-'s to balance charge 3. Add OH^-'s as needed to balance <u>charge</u> 4. Add H_2O's to balance hydrogens 5. Check at the end to make sure: <ol style="list-style-type: none"> a. Charges balance b. Atoms balance

Standard Reduction (Electrode) Potentials at 25° C (OWL)

Half-cell reaction	E_o (volts)
$F_2 + 2e \rightarrow 2F^-$	2.87
$Ce^{4+} + e \rightarrow Ce^{3+}$	1.61
$MnO_4^- + 8 H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$	1.51
$Cl_2 + 2e \rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14 H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2 + 4H^+ + 4e \rightarrow 2H_2O$	1.229
$Br_2 + 2e \rightarrow 2Br^-$	1.08
$NO_3^- + 4H^+ + 3e \rightarrow NO + 2H_2O$	0.96
$2Hg^{2+} + 2e \rightarrow Hg_2^{2+}$	0.920
$Hg^{2+} + 2e \rightarrow Hg$	0.855
$O_2 + 4 H^+ (10^{-7} M) + 4e \rightarrow 2H_2O$	0.82
$Ag^+ + e \rightarrow Ag$	0.799
$Hg_2^{2+} + 2e \rightarrow 2Hg$	0.789
$Fe^{3+} + e \rightarrow Fe^{2+}$	0.771
$I_2 + 2e \rightarrow 2I^-$	0.535
$Fe(CN)_6^{3-} + e \rightarrow Fe(CN)_6^{4-}$	0.48
$Cu^{2+} + 2e \rightarrow Cu$	0.337
$Cu^{2+} + e \rightarrow Cu^+$	0.153
$S + 2H^+ + 2e \rightarrow H_2S$	0.14
$2H^+ + 2e \rightarrow H_2$	0.0000
$Pb^{2+} + 2e \rightarrow Pb$	-0.126
$Sn^{2+} + 2e \rightarrow Sn$	-0.14
$Ni^{2+} + 2e \rightarrow Ni$	-0.25
$Co^{2+} + 2e \rightarrow Co$	-0.28
$Cd^{2+} + 2e \rightarrow Cd$	-0.403
$Cr^{3+} + e \rightarrow Cr^{2+}$	-0.41
$2H_2O + 2e \rightarrow H_2 + 2OH^- (10^{-7} M)$	-0.41
$Fe^{2+} + 2e \rightarrow Fe$	-0.44
$Cr^{3+} + 3e \rightarrow Cr$	-0.74
$Zn^{2+} + 2e \rightarrow Zn$	-0.763
$2H_2O + 2e \rightarrow H_2 + 2OH^-$	-0.83
$Mn^{2+} + 2e \rightarrow Mn$	-1.18
$Al^{3+} + 3e \rightarrow Al$	-1.66
$Mg^{2+} + 2e \rightarrow Mg$	-2.37
$Na^+ + e \rightarrow Na$	-2.714
$K^+ + e \rightarrow K$	-2.925
$Li^+ + e \rightarrow Li$	-3.045