

## Chapter 19 Electrochemistry Math Summary

### Relating Standard Cell Potential to Standard Half Cell Potentials

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

### Relating Half Cell Potentials when Written in Opposite Directions

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

### Relating Standard Cell Potentials to $\Delta G$

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

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

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 4.9)**

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 <sub>2</sub> , O <sub>2</sub>
2.	Monatomic ions	= charge	F <sup>1-</sup> , Na <sup>1+</sup> , Fe <sup>3+</sup>

**IN COMPOUNDS**

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

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 it's oxidation number = "x", and solve for "x" such that the ox. #'s = actual charge.

**Balancing Redox: Simple Cases where all Reactants and Products are Provides**

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

**Standard Reduction (Electrode) Potentials at 25° C (Appendix 6, shortened)**

Half-cell reaction	E <sub>o</sub> (volts)	Half-cell reaction	E <sub>o</sub> (volts)
F <sub>2</sub> + 2e → 2F <sup>-</sup>	2.87	Pb <sup>2+</sup> + 2e → Pb	-0.126
Ce <sup>4+</sup> + e → Ce <sup>3+</sup>	1.61	Sn <sup>2+</sup> + 2e → Sn	-0.136
MnO <sub>4</sub> <sup>-</sup> + 8 H <sup>+</sup> + 5e → Mn <sup>2+</sup> + 4H <sub>2</sub> O	1.507	Ni <sup>2+</sup> + 2e → Ni	-0.257
Cl <sub>2</sub> + 2e → 2Cl <sup>-</sup>	1.36	Co <sup>2+</sup> + 2e → Co	-0.277
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> + 14 H <sup>+</sup> + 6e → 2Cr <sup>3+</sup> + 7H <sub>2</sub> O	1.33	Fe <sup>2+</sup> + 2e → Fe	-0.447
O <sub>2</sub> + 4H <sup>+</sup> + 4e → 2H <sub>2</sub> O	1.229	Cr <sup>3+</sup> + 3e → Cr	-0.74
Br <sub>2</sub> + 2e → 2Br <sup>-</sup>	1.066	Zn <sup>2+</sup> + 2e → Zn	-0.7618
Ag <sup>+</sup> + e → Ag	0.7996	2H <sub>2</sub> O + 2e → H <sub>2</sub> + 2OH <sup>-</sup>	-0.8277
Fe <sup>3+</sup> + e → Fe <sup>2+</sup>	0.5355	Al <sup>3+</sup> + 3e → Al	-1.662
I <sub>2</sub> + 2e → 2I <sup>-</sup>	0.48	Mg <sup>2+</sup> + 2e → Mg	-2.37
Cu <sup>2+</sup> + 2e → Cu	0.3419	Na <sup>+</sup> + e → Na	-2.71
2H <sup>+</sup> + 2e → H <sub>2</sub>	0.0000	K <sup>+</sup> + e → K	-2.95
Cu <sup>2+</sup> + e → Cu <sup>+</sup>	0.153	Li <sup>+</sup> + e → Li	-3.05

## 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 (19.1, See Section 4.9 to review)**

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 <sub>2</sub> , O <sub>2</sub>
2.	Monatomic ions	= charge	F <sup>1-</sup> , Na <sup>1+</sup> , Fe <sup>3+</sup>

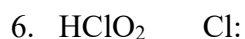
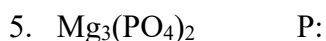
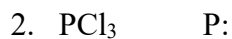
## IN COMPOUNDS

3.	Group 1A	= +1	NaCl, KNO <sub>3</sub>
4.	Group 2A	= +2	MgO
5.	Fluorine	= -1	HF, ClF
6.	Hydrogen	= +1	H <sub>2</sub> O
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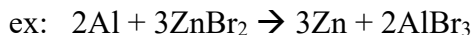
**The sum of all oxidation numbers of all elements = charge on substance.**

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

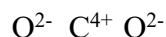
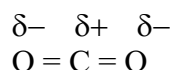
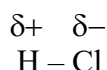
Find Ox #'s for



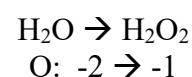
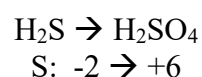
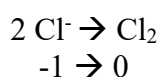
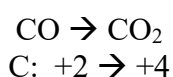
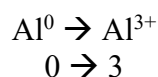
## 19.1 Redox Reactions (Review: 4.9)

Recognizing Redox Reactions:

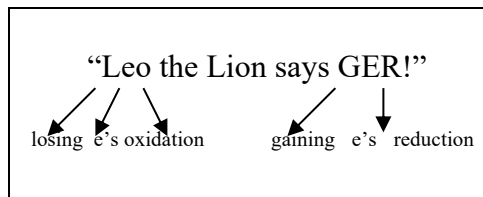
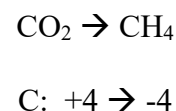
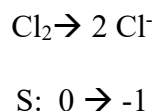
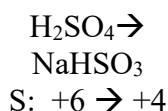
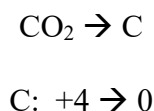
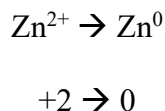
- Any reaction in which an **elemental** substance is involved is always a redox reaction
  - The element can be on either reactant or product side, or both
- Any reaction involving a Change in “oxidation number” is a redox reaction (review 5.4)
  - Oxidation numbers count charges in molecular as well 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

- Oxidation: loss of e's
  - Ox # increases (more positive or less negative)



- Reduction: gain of e's
  - Ox # is “reduced” (less positive or more negative)



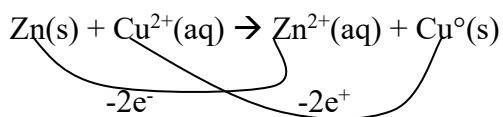
- All redox reactions require both an electron giver (the thing that is oxidized) and an electron taker (the thing that is reduced)
  - Essentially a redox reaction involves a competition for a limited supply of electrons
  - In the example shown, there aren't enough electrons for both Al and Zn to be in their reduced zero-charge form. One or the other must be in its electron-deficient oxidized form
 
$$2\text{Al} + 3\text{ZnBr}_2 \rightarrow 3\text{Zn} + 2\text{AlBr}_3$$
  - That  $\text{Al}^{3+}$  ends up oxidized and  $\text{Zn}^0$  ends up reduced suggests that Zn has a higher electron-love than Al
  - Competition for limited electrons not unlike acid/base competition for limited  $\text{H}^+$ 's
 
$$2\text{Al} + 3\text{ZnBr}_2 \rightarrow 3\text{Zn} + 2\text{AlBr}_3$$

4. “Oxidizing Agent” or “Oxidant”: causes something else to be oxidized
  - is itself reduced
  - $\text{Zn}^{2+}$ , 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  $\text{Zn}^{2+}$  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

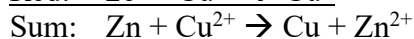
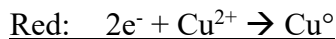
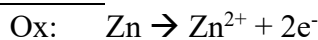
1.  $2\text{Na} + 2\text{HCl} \rightarrow 1\text{H}_2 + 2\text{NaCl}$
2.  $2\text{KMnO}_4 + 6\text{NaCl} \rightarrow 2\text{MnO}_2 + 3\text{Cl}_2$  (some  $\text{H}_2\text{O}$ ,  $\text{KOH}$ ,  $\text{NaOH}$  also involved)

Half Reactions, Redox, and Balancingn (19.2 )



- both oxidation and reduction must occur
- electrons must balance

Half Reactions

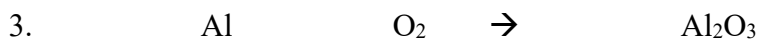
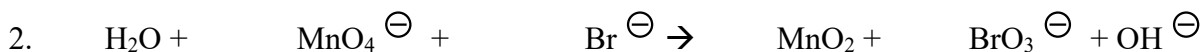


Suppose:  $\text{Zn}^{2+}$  reacts with Na. Draw the oxidation and reduction half reactions, and balance them for electrons. Combine them to make the sum redox reaction:

ReductionOxidationNet SumBalancing Redox

- Identify oxidation numbers for redox actors
- Set coefficients for them so that the **#e's released = #e's accepted**
  - focus completely on the atoms whose oxidation numbers change
- Then balance any redox spectators
- 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

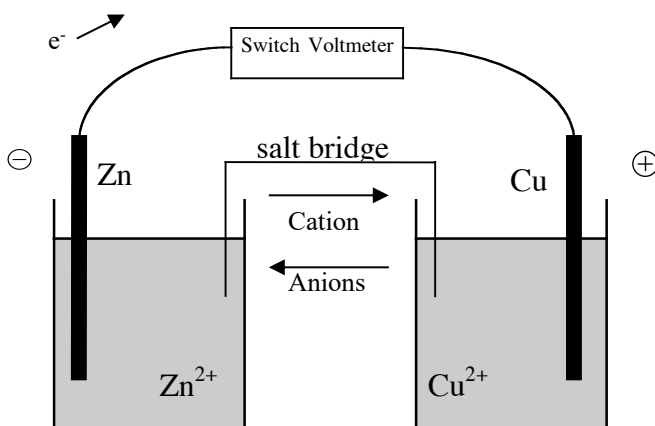
Balance (Test Level)

**Electrochemical Cells** (19.2)

Example:  $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$       2 electron flow

- 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

Setup2 Solid metals = “electrodes”

- electrodes can be metal, plates or wires, or graphite or some other materials: (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 ( $\text{Cu}^0$  forming)
  - positive sign on battery

Two “Half Cells” and “Half Reactions”

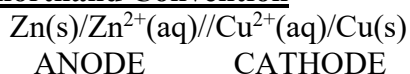
- “Anode” side = Where the oxidation half reaction occurs ( $\text{Zn} \rightarrow \text{Zn}^{2+}$  beaker)
- “Cathode” side = Where the reduction half reaction occurs ( $\text{Cu}^{2+} \rightarrow \text{Cu}$  beaker)

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 (not for test)

- Special cells when H<sub>2</sub> gas is produced
- Many types use conductive graphite electrodes on which surface redox half-reactions occur
- “Dry cells” involving thick paste mixtures rather than any solvent (many batteries)

**Electrochemical Cells and Voltage** (19.3)

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

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

$E^{\circ}_{\text{cell}}$  = **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:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidation}} + E^{\circ}_{\text{reduction}}$$

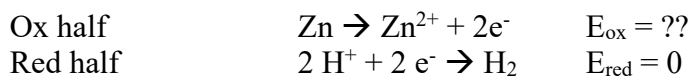
Anode                  Cathode

Each half reaction has an  $E^{\circ}$ , relative to self-defined **reference half reaction**



Show Appendix 6.1, APP-26, Standard Redox Potentials

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



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

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



**Using  $E^\circ_{\text{cell}}$  and known Half Potentials (19.3)**

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

1. Tables list reduction halves  $E^\circ_{\text{red}}$  (Appendix 6.1 App-26)

$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	+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.  $E^\circ_{\text{ox}} = - E^\circ_{\text{red}}$

Red: $\text{Zn}^{2+} \rightarrow \text{Zn}$	$E^\circ_{\text{red}} = - 0.76\text{V}$
Ox: $\text{Zn} \rightarrow \text{Zn}^{2+}$	$E^\circ_{\text{ox}} = + 0.76$

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

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

3. Key skill: Given known halves, deduce  $E^\circ_{\text{cell}}$ .

Ex:  $\text{Ni} + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{Ni}^{2+}$  Balance and find  $E^\circ_{\text{cell}}$

4. Stoichiometry coefficients don't matter to  $E^\circ$ 's

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

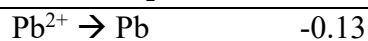
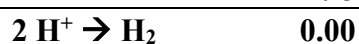
5. Key skill: Given an overall  $E^\circ_{\text{cell}}$  and one known or knowable half potential ( $\text{Cu}^{2+}$  redn = +0.34V), calculate the half potentials for the other half (without needing or having table access).



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

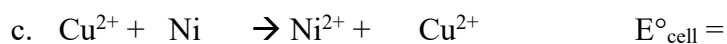
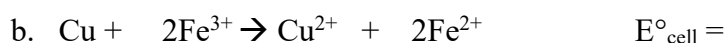
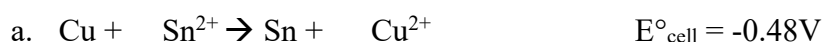
Find  $E^\circ_{\text{ox}}$  for:  $\text{Sn} \rightarrow \text{Sn}^{2+}$

6. **Hydrogen Reference:** All redox half-reaction potentials are relative to  $\text{H}^+$  reduction ( $E^\circ_{\text{red}}=0$ ) or  $\text{H}_2$  oxidation ( $E^\circ_{\text{ox}}=0$ ) (19.5)



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

Q: Which of the following are favorable redox reactions?



Logic: 1. Find  $E^\circ_{\text{cell}}$  from  $E^\circ_{\text{ox}}$  and  $E^\circ_{\text{red}}$   
 2. Check if  $E^\circ_{\text{cell}}$  is positive or negative.

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
  - Neutral:  $\text{F}_2$  loves to be reduced (gain electrons), so has best reduction potential
  - Anions:  $\text{F}^-$  holds negative charge best, so has the worst anion oxidation potential
  - Lithium has low electron love, so is easily oxidized
  - Because unattractive towards electrons, lithium cation has poor oxidation potential

Q1: Based on table, rank the electron affinities for Cu,  $\text{H}_2$ , Ni, and Pb

Q2: Which would be a stronger oxidizing agent (stealer of e's),  $\text{Cu}^{2+}$  or  $\text{Ni}^{2+}$  ?

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

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  $E^\circ_{\text{red}}$   $\Rightarrow$ 
  - a. more easily reduced
  - b. stronger love for e's
  - c. stronger oxidizing agent

Right Side

- 1 **Reduced Form** (more electrons)
- 2 **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  $E^\circ_{\text{red}}$   $\Rightarrow$ 
  - 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  $\text{Cu}^{2+}$ ?
- d. Which will react with  $\text{Cu}^0$ ?

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	
		$\text{Pb}^{2+} \rightarrow \text{Pb}$	-0.13	
		$\text{Ni}^{2+} \rightarrow \text{Ni}$	-0.25	
		$\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$	-0.74	

- Strongest Oxidizing agent: top left (max e- love)
- Strongest Reducing agent: bottom right (min e- love)

### Odds and Ends

1. 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

a. What species would react with  $\text{Pb}^{2+}$ ?

b. What species would react with Pb?

2. For two species to react, one must be in reduced form (reducing agent), and the other in oxidized form (oxidizing agent)

c. What of the following species could react with  $\text{Cu}^{2+}$ ?



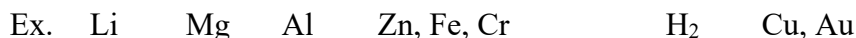
d. What of the following species could react with  $\text{Cr}^{2+}$ ?



3. Given redox chart, rank electron love and basically predict which reactions are or aren't favorable
4. 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)



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

- A real cell needs an oxidation half reaction, so one of the reductions must be reversed.
- 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  $E^\circ_{\text{cell}}$

### Examples

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

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

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 A:  $\text{X} + \text{Y}^{2+} \rightarrow \text{Y} + \text{X}^{2+}$  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 B:  $Q + P^{2+} \leftarrow P + Q^{2+}$  Non-reaction (Reactant-favored redox).

- In other words, no reaction when Q is mixed with  $P^{2+}$ .
- Between P and Q:
  - a. Which element loves electrons more?
  - b. What thing is the strongest reducing agent?
  - c. Which thing is the strongest oxidizing agent?
  - d. 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.**

- The side with the weaker reducing agent and weaker oxidizing agent.

### Miscellaneous Problems

1.  $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$   $E^\circ = 0.32V$ 
  - What is the “reduction potential” for  $Fe^{2+}$  ( $Fe^{2+} \rightarrow Fe^\circ$ ) given the above potential, and given that:  $Zn^{2+} \rightarrow Zn$   $E^\circ_{red} = -0.76$
  
2. Find  $E^\circ$  for product favored reaction involving the following, and balance the reaction
 

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

  - a. keep more favorable one as reduction
  - b. reverse less favorable to make it an oxidation
  - c. sum  $E^\circ_{ox}$  and  $E^\circ_{red}$
  - d. adjust coefficients to balance e’s
  
3. Ditto for  $Br_2 \rightarrow 2 Br^-$  +1.06  
 $Zn^{2+} \rightarrow Zn$  -0.76

4. Reduction potentials for  $\text{Ni}^{2+}$  and  $\text{Sn}^{2+}$  are  $-0.25\text{V}$  and  $-0.16\text{V}$ .
- Which of  $\text{Ni}^{2+}$  and  $\text{Sn}^{2+}$  is a stronger oxidizing agent?
  - Which of Ni and Sn is a stronger reducing agent?
  - Would either or both of Ni and Sn react with  $\text{H}^+$ ?

### Periodic Table-Based Predictions

5. Predict/Rank  $E^\circ_{\text{ox}}$  for:

Li                      Mg                      Fe                       $\text{H}_2$                       Ag

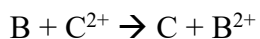
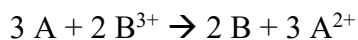
6. Rank/predict  $E^\circ_{\text{red}}$  for

$\text{Li}^+$                        $\text{Mg}^{2+}$                        $\text{Fe}^{2+}$                        $\text{H}^+$                        $\text{Ag}^+$

7. Rank  $\text{F}_2$   $\text{Cl}_2$   $\text{I}_2$  as oxidizing agents.
8. Rank  $\text{F}^-$   $\text{Cl}^-$   $\text{I}^-$  as reducing agents.

### Activity Series

Reducing Activity \_\_\_\_\_ Electron Love



9. Rank “activity” of A, B, C, D
10. Rank “activity” of  $\text{A}^{2+}$ ,  $\text{B}^{3+}$ ,  $\text{C}^{2+}$ ,  $\text{D}^{2+}$
11. Rank electron love

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

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

13. Which species react with  $\text{Zn}^0$ ?

14. Which element loves e's the most?

15. Which element loves e's the least?



a. Product favored or not?

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



**Relating  $E^\circ_{\text{cell}}$  to  $\Delta G^\circ$  and  $K$ . Chemical Energy and Electrical Work** (19.4)

	$\Delta G$	$E^\circ_{\text{cell}}$	$K$
Product Favored	neg	pos	large
Reactant Favored	pos	neg	small
**Equilibrium	0	0	1

$\Delta G^\circ$  and  $E^\circ_{\text{cell}}$  have opposite signs, but are related

- both provide measurements for the favorability or unfavorability of a reaction
- obviously  $E^\circ_{\text{cell}}$  is more limited, to redox reactions
- $K$  is also related, since it too relates to how favorable or unfavorable a reaction is
- $\Delta G^\circ$  = “free energy” available to do be released and do work
- $E^\circ_{\text{cell}}$  also reflects the amount of energy that is released to do work when a favorable redox transfer occurs
  - The “free energy” in an electrical cell is really the free energy to do the work of moving electrons and to the work that flowing electricity can do

Key Formula for relating  $\Delta G^\circ$  and  $E^\circ_{\text{cell}}$

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

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

$n$  = 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  $\Delta G$  in kJ/mol

Math derivation (not for test):

Units

$$F = \frac{96,500\text{C}}{\text{mole } e^-}$$

$$V = \frac{J}{C} \text{ so } C = \frac{J}{V}$$

$C$  = coulomb, unit of electricity, amount of charge

Substituting

$$F = \frac{96,500\text{J}}{\text{mole } e^- \cdot V}$$

$$F = \frac{96.5 \text{ kJ}}{\text{mole } e^- \cdot V}$$

Thus when “ $n$ ” is moles of electrons, and  $E^\circ_{\text{cell}}$  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

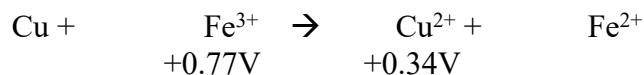
- Force for moving electrons and charge
- Not all Coulombs of charge have the same energy/power/force/ability to do work
- Just like dropping a brick from one cm has less force than dropping it from two meters high

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

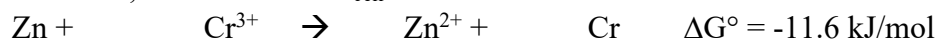
Watt = amount of energy

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

1. Balance the reaction, and find  $\Delta G^\circ$  given the reduction potentials shown



2. Balance the reaction, and calculate  $E^\circ_{\text{cell}}$ .



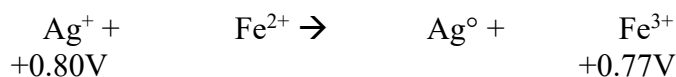
3. If the reduction potential for  $\text{Zn}^{2+}$  is  $-0.76\text{V}$ , what is the reduction potential for  $\text{Cr}^{3+}$ ?

**Cell Voltage and K** Voltage and K are also linked!!

- The more favorable and positive  $E^\circ_{\text{cell}}$ , 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)

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

4. Calculate K, given reduction potentials.



**The Effect of Concentration on Cell Potential: Voltages when Concentrations are not 1.0 M** (19.6)

- $E^\circ$  assumes 1.0 M concentrations for any soluble species (and 1.0 atm pressure for any gas)
  - rarely actually true!
- 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,  $E_{\text{actual}} = 0 \text{ V}$

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

- Calculate actual voltage for  $\text{Mg}/\text{Mg}^{2+}(0.10\text{M})//\text{Cu}^{2+}(0.001\text{M})/\text{Cu}$   
given the following reduction potentials:

$$\text{Mg}^{2+} = -2.37\text{V}$$

$$\text{Cu}^{2+} = +0.34\text{V}$$

Logic Steps

- Calculate actual voltage for  $\text{Cu}/\text{Cu}^{2+}(1.0\text{M})//\text{Ag}^+(0.032\text{M})/\text{Ag}$

$$E_{\text{red}}^\circ$$

$$\text{Ag}^+ \quad +0.80\text{V}$$

$$\text{Cu}^{2+} \quad +0.34\text{V}$$

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

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

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

Using Nernst Equation to Calculate the Cell Potential and Equilibrium Equation (not for test)

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

At equilibrium:

a.  $E_{\text{actual}} = 0 \text{ V}$

b.  $Q=K$

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

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

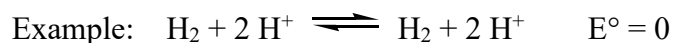
Finding  $E^{\circ}$  given  $K$

Rearranged:  $\log K = nE^{\circ}_{\text{cell}} / (0.0592)$

Finding  $K$  given  $E^{\circ}_{\text{cell}}$

“Concentration cells”, pH meters, and neurons:

- anode and cathode use the same chemicals, but with ions at different concentrations
- at equilibrium, the concentrations would be equal, so the voltage drive is to equalize



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

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

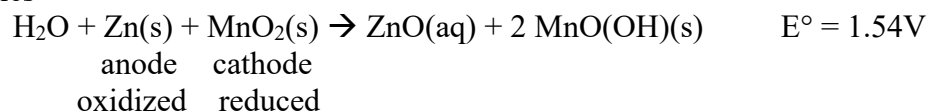
- pH meter: dip meter with known  $[\text{H}^+]$  into a solution, measured voltage reflects solution  $[\text{H}^+]$
- neurons: The  $\text{H}^+$  concentration differs inside and outside cell membranes. This creates a voltage which is the key for nerve sensation

**Common Batteries** (19.7-9)

## A. Primary: Nonrechargeable

- run till concentration achieves equilibrium = dead = toss

## 1. Alkaline batteries



- flashlights, radio, toys, Jasperse insulin pump, Jasperse blood testers, tooth brush, etc.

2. Lithium batteries  $\text{Li(s)} + \text{CoO}_2\text{(s)} \rightleftharpoons \text{LiCoO}_2\text{(s)} + \text{energy}$   $E^\circ = 3.4\text{V}$ 

- Lithium is actually in a polymer with carbon graphite)

Pros:

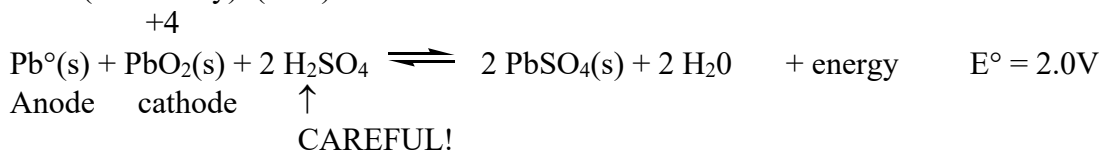
- Big voltage → good for fueling energy eaters, like laptops, cameras, cell phones
- Light weight

Cons

- More expensive

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

## 1. Lead-acid (car battery) (19.8)

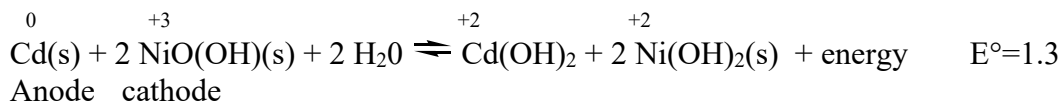


Leakage caused corrosion!

- 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

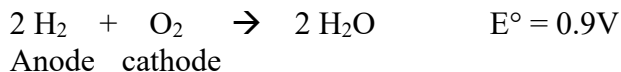
2. NiCad  $E^\circ=1.3$ 

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



- reaction can reverse upon treatment with electrical energy

## 3. Fuel Cell: continuous feed of reactants from outside to electrodes (19.9, interest, not test)

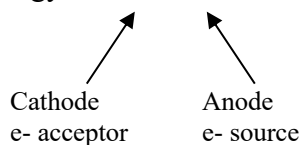
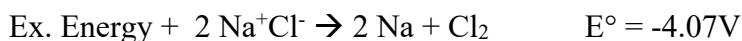


- $\text{H}_2 + \text{O}_2$  light, so good fuels, high energy efficiency
- Spaceships: 500 pounds of fuel enough energy for 11 days
- Dream: come up with way to use solar/wind energy to produce  $\text{H}_2$  from water
- Fuel cells for cars: Need to “stack” lots to multiply the power

**Electrolysis: Using outside electricity to drive unfavorable redox reactions** (19.18)

- key process in recharging rechargeable batteries
- key route to elements not found in nature: metals, H<sub>2</sub>, Cl<sub>2</sub>,...

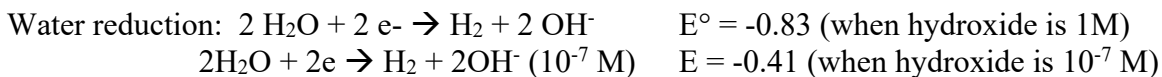
A. Electrolysis of Molten Salts (“molten” = melted, pure liquid salts in absence of solvent, super hot!!)



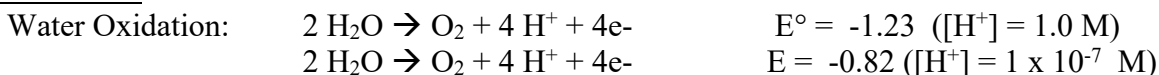
- products must be kept separate so can't react

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



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

Oxidation/Anode

**C. Electroplating:** metal cation → 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, corrosions are often electroplated with a coating that is resistant to air, rain, and acid.

**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  $\text{AlCl}_3$  at 10.0A current?

2. At 3.2A, how long will it take to make 10g of Zn (65.4 g/mol) from  $\text{ZnBr}_2$ ?

3. What current in amps is required to make 10 grams of  $\text{Cl}_2$  (71 g/mol) from  $\text{AlCl}_3$  in one hour?

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
 
$$O_2 + 4H^+ \rightarrow 2 H_2O \quad E^\circ_{red} = +1.23V \text{ very good under standard conditions!!}$$
- Most metals can oxidize/corrode, 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:

1. Corrosion often speeded by  $H^+$  and/or ionic salts that acidity water
2. Gold has always been valued because unlike other oxidizable metals, it retains it's elemental form and it's lustrous golden elemental surface appearance.
3. 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.
4. 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

1. 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
2. “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 20 Nuclear Chemistry Math Summary

### Particles Involved in Nuclear Reactions, either as Nucleons, Emitted particles or Particles that React with a Nucleus and Induce a Decay

(Memorize these for Test)

-the first three, alpha, beta, and positrons are the crucial ones for balancing radioactive nuclear decay reactions

$\frac{4}{2}\text{He}$ $\alpha$ -particle (alpha)	$\frac{0}{0}\gamma$ gamma
$\frac{0}{-1}\text{e}$ $\beta$ -particle (beta), electron	$\frac{1}{0}\text{n}$ neutron
$\frac{0}{+1}\text{e}$ positron	$\frac{1}{1}\text{H}$ proton

### Radioactive Decay Math

$t = (t_{1/2}/0.693) \ln (A_o/A_t)$     When solving for time, given half life and quantities of material

$\ln (A_o/A_t) = 0.693 (t /t_{1/2})$     When solving for the amount of material left after a given time, given the half life

Handling “ $\ln y = x$ ” on calculator, when you know “ $x$ ” but want to solve for “ $y$ ”: enter “ $x$ ”, then hit your “ $e^x$ ” button.

### Mass Defect/Binding Energy Math

Proton mass: 1.00783

Neutron mass: 1.00867

$$E = \Delta mc^2$$

$$\Delta m = (\text{sum mass of protons plus neutrons}) - \text{actual mass}$$

- The binding energy will depend on the  $\Delta m$  difference between the summed weight of the protons and neutrons minus the actual mass of the nucleus.
- $\Delta m$  in terms of kilograms (you’ll normally need to convert from grams to kg)
- The energy answer from the formula comes out in terms of Joules, not kJ; you’ll routinely need to convert from J to kJ to fit the answers



## Ch. 21 Nuclear Chemistry

1. Some rules for chemical reactions that do not apply to nuclear reactions:
  - a. Balanced reactions: the same atoms that go into a reaction come out
  - b. Conservation of mass (no mass is gained or lost)
  - c. Conservation of energy
2. In nuclear reactions:
  - a. Nuclei do change! ( $C \rightarrow N$ ,  $U \rightarrow Ba$ , etc.)
  - b. Mass does change (slightly)  $\Rightarrow$  large energy changes
  - c. Energy is not conserved: energy is produced
    - Mass is actually converted to energy via Einstein's  $E=mc^2$
    - The real conservation is of energy/mass, but in nuclear reactions mass can be converted into energy

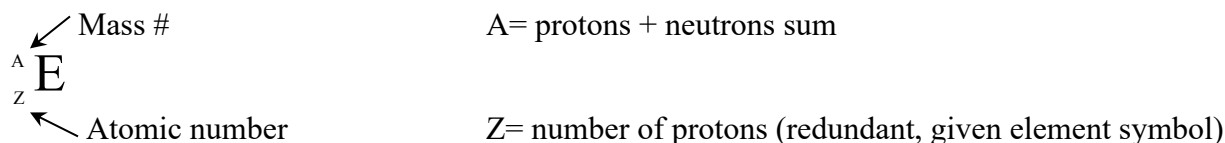
Applications of Nuclear Energy

1. Energy source
  - ~20% of US electricity, ~17% world-wide
  - cheap! Efficient
  - no greenhouse gases: environmentally 'clean', no acid rain, etc.
  - Currently, all the nuclear waste from one reactor can be stored in one barrel of "glass"
2. Medicinal
  - a) diagnostic tracers, "imaging"
    - PET: position emission tomography
    - thyroid, heart, tumors, bone studies, brain imaging, blood flow tracking
  - b) therapy: anti-cancer radiation therapy
3. Radioactive tracers, labelling
  - Incorporating radioactive nuclei into reactive molecules enables scientists to figure out which atoms go where in chemical and biochemical reactions
  - This enables researchers to unravel many biological pathways
4. Age dating
  - $^{14}C$  for archeological dates: recent several thousand years while people have been around (Carbon dating)
  - K/Ar dating for geological dates (dates for rocks, on the order of millions or billions rather than thousands of years)
5. Food irradiation: kill/retard Bacteria, molds, yeast (ala pasteurization)
6. Bombs!!
  - Fission: original WWII uranium bombs, in which big uranium nuclei break into smaller nuclei
  - Fusion (Hydrogen bomb): more powerful subsequent cold-war developed bombs that are much, much more destructive. Involve small hydrogen nuclei fusing into larger nuclei
7. Sun energy. All of the energy from the sun is produced by hydrogen and helium fusion.
  - All of the energy that we live on originally began with the sun
  - Plants harvest solar energy via photosynthesis
  - People and animals harvest energy by eating plants or by eating animals that ate plants
  - The solar energy harvested by plants also ends up being converted to fossil fuels and firewood

## Radioactivity: Spontaneous Disintegration of Nucleus (21.1,2)

- although spontaneous, this may still be very slow. Rates vary widely, which is good.

## A. Nuclear Review: Symbols for “Nuclide”



- Number of protons = Z (atomic number)
- Number of neutrons = A (mass number) – Z (number of protons)
- Number of electrons = Number of protons for a neutral atom
  - For an anion, negative charge means more electrons than protons
  - For a cation, the positive charge means fewer electrons than protons

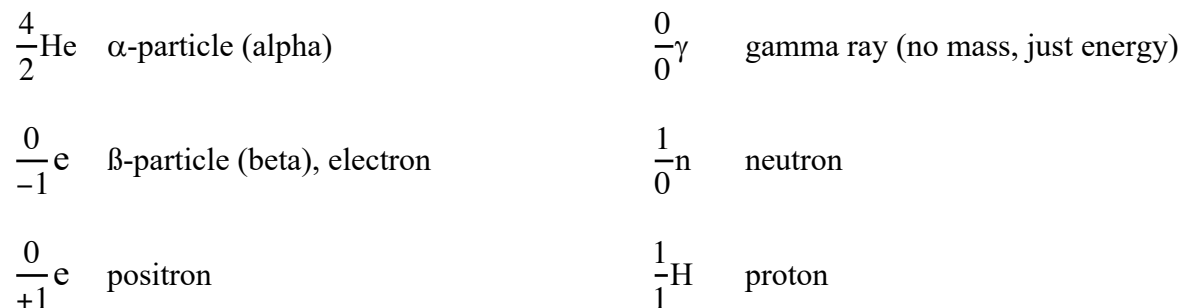
“isotopes”: nuclei that have the same number of protons but differing number of neutrons

- $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{14}\text{C}$  all have six protons
- Stability often depends on the neutron/proton ratio, so frequently different isotopes will have different stability

“radioisotopes”: particular isotopes that spontaneously disintegrate and release radiation

Shorthands:  $^{12}_6\text{C} = {}^{12}\text{C} = \text{C12} = 12\text{C}$

## B. Common “Particles” involved in Radioactivity and Nuclei (memorize these for test)



- Memorize names, symbols, constitution
- Crucial in balancing nuclear reactions
- The radiation emitted by radioactive elements is normally alpha, beta, or gamma. Positron emission and neutron emission is more rare.
  - Protons and neutrons are often involved when nuclei are being intentionally bombarded
- Different radiation has different penetrating power. (20.8) Biological impact depends on:
  - The number or rays/particles that strike
  - The energy and penetration depth of the rays
  - Whether the radiation originates inside or outside the body

$\gamma$ <b>Max damage, due to high energy, deep penetration</b>	$\beta$ Penetrate only a few mm	$\alpha$ Little penetration, only irritates outer skin. But bad if generated internally.
--	---------------------------------	--

**Nuclear Reactions: Equations and Balancing**

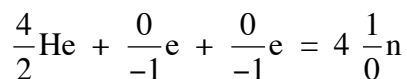
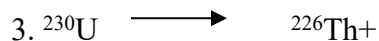
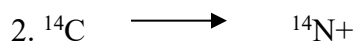
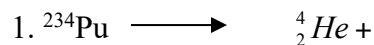
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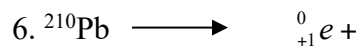
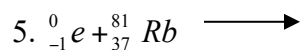
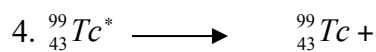
1. balance mass sum (top)
2. balance charge sum (bottom)

**Five Types of Radioactive Reactions (Spontaneous)**

	<u>Isotope Change</u>	<u>Effect on n/p ratio</u>	
1. Alpha emission	$\frac{A}{Z} \rightarrow \frac{4}{2}\text{He} + \frac{A-4}{Z-2}$ A - 4 change Z - 2 change	$\frac{n-2}{p-2}$	
2. Beta emission	$\frac{A}{Z} \rightarrow \frac{0}{-1}\text{e} + \frac{A}{Z+1}$ no change increase	$\frac{n-1}{p+1}$	Lower Neutron becomes a proton
3. Positron emission	$\frac{A}{Z} \rightarrow \frac{0}{+1}\text{e} + \frac{A}{Z-1}$ no change decrease	$\frac{n+1}{p-1}$	Higher Proton becomes a neutron
4. Electron capture	$\frac{0}{-1}\text{e} + \frac{A}{Z} \rightarrow \frac{A}{Z-1}$ no change decrease	$\frac{n+1}{p-1}$	Higher Proton becomes a neutron
5. Gamma emission	$\frac{A}{Z} \rightarrow \frac{0}{0}\gamma + \frac{A}{Z}$ no change no change	No change	

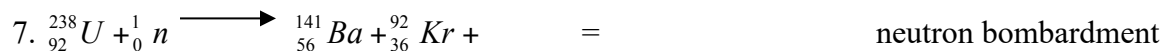
- Radioactive Series: many decays give unstable daughter nuclei, which then undergo subsequent serial decays
- A very common sequence when the n/p ratio is too high is emission of one  $\alpha$  and two  $\beta^-$  particles (in any sequence)
- This results in the effective removal of 4 neutrons

**Fill in the Holes, Name the process**



**Artificial Transmutations:** The human-induced conversion of one nucleus into another by Bombardment with  ${}_0^1n$  or other nuclei. (21.5)

1. Key: reactions must still balance in the same way.
2. Often products are accompanied by production of side particles, often multiple neutrons
3. Few radioactive nuclei are still found in nature. Most fast-decay nuclei used for research or medicine are made by bombardment.



**The Stability of Atomic Nuclei (21.4)**

## A. Physics background

## a. 3 fundamental forces

1. gravity
2. electrostatic attraction: opposite charges attract
3. “strong nuclear force”

b. **proton-proton repulsion destabilizes** all nuclei except hydrogen **BAD**

- This repulsion increases sharply with increasing number of protons
- In other words, as nuclei increase in atomic number, this destabilizing repulsion increases exponentially
- This is a destabilizing electrostatic force
- If proton-proton repulsion is destabilizing, why do nuclei exist at all for atoms other than hydrogen?

c. **“strong nuclear force”** between protons or neutrons **GOOD**

- This attracts nuclides, holds nucleus together
- Unknown how the strong nuclear force works. It’s existence and strength is really known by deduction!
- The neutron/proton ratio increases with larger nuclei.
  - This enables the strong nuclear force to increase at a pace that can balance the proliferating proton-proton repulsion
- Beyond atomic-number of 83, it becomes impossible for the nuclear force to keep up with the destabilizing proton-proton repulsion, so nuclei cease to be stable.

**Fig. 20.2, 21.2 Brown**

B. Decay Patterns: The Band of Stability Target Ratio: A range of n/p ratios that appropriately balance the electrostatic repulsion and the nuclear attraction and give stable nuclei

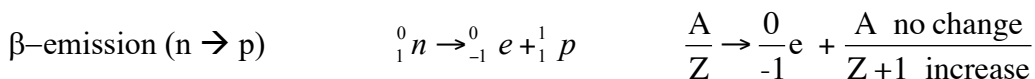
1. Rule of 83: Atoms/nuclei with atomic number of  $Z > 83$  are radioactive
  - nuclear force can’t keep up!
  - most elements  $Z < 83$  have at least one stable isotope ( ${}_{43}\text{Tc}$ ,  ${}_{61}\text{Pm}$ )
  - **$Z > 83$  emit  $\alpha$**  to reduce  $Z$

Normal solution: For unstable nuclei with  $Z > 83$ , **alpha emissions** normally occurs, to reduce the atomic number and move it toward stability

2. For atoms with  $Z < 83$ , but above the band of stability: **atoms whose n/p ratio is too high**

- Conversion of a neutron into a proton would help

Normal solution: For nuclei whose n/p ratio is too high, **beta emissions** normally occurs, to reduce the n/p ratio by converting a neutron into a proton

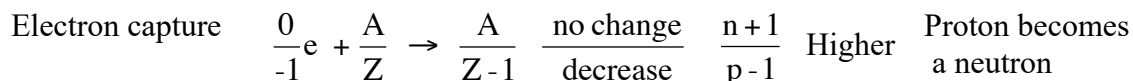
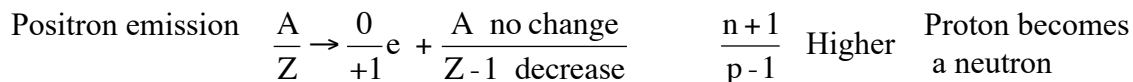


3. For atoms with  $Z < 83$ , but below the band of stability: **atoms whose n/p ratio is too low**

- Conversion of a proton into a neutron would help

Normal solution: For nuclei whose n/p ratio is too low, either **positron emission or electron capture** normally occurs, to increase the n/p ratio by converting a proton into a neutron

- Electron capture tends to be more likely for higher-Z elements



**Practical: How do I recognize whether a nucleus is likely to be stable or not? And if it isn't, how do I predict what it will do?**

1. **Check Z. Is  $Z > 83$ ?** If so, then **expect alpha emission**. If not, proceed to step two.
2. **Compare the n/p ratio to the ratio found in the periodic table for the same atom.**
3. If the **n/p ratio is similar**, it's probably a **stable** nucleus.
4. If the **n/p ratio is significantly higher** than in the periodic table, **expect beta emission**.
5. If the **n/p ratio is significantly lower** than in the periodic table, then **expect either positron emission or electron capture**.

- Note: There are some not-well-understood kind of stability pattern
- Pairing seems to be preferred, although it's not understood why
  - Even numbers of protons and even numbers of neutrons seem to be preferred, all else being equal

Problems: Predict how the following would decay by  $\alpha$ ,  $\beta$ , or positron emission, or by electron capture. Then draw the nuclide produced.

1.  $^{40}\text{Cl}$

2.  $^{134}\text{Ba}$

3.  $^{237}_{93}\text{Np}$



**Binding Energy** (21.3)

- the mass of an actual nucleus is always less than the sum of its component neutrons and protons
- The **missing mass ( $\Delta m$ )** is called the “**mass deficit**”.

$$\Delta m = (\text{mass sum of protons} + \text{neutrons}) - \text{actual nuclear mass}$$

$${}^1_1\text{proton} \quad 1.00783 \quad \quad \quad {}^1_0\text{neutron} \quad 1.00867$$

- The **mass deficit ( $\Delta m$ )** equals the “**nuclear binding energy**” = “**strong nuclear force**”

$$E = \Delta mc^2$$

$$\begin{array}{l} \Delta m \text{ in kg (convert from grams to kg)} \\ E \text{ in J (convert to kJ)} \end{array}$$

- Get answers in either kJ/mol (of nucleus) or kJ/mole nucleon”
  - The number of “nucleons” is the sum of protons and neutrons

4. What is the binding energy in kJ/mol for  ${}^{16}_8\text{O}$ ?

$$\text{Given: } {}^{16}_8\text{O} \quad 15.978 \quad \quad \quad {}^1_1\text{proton} \quad 1.00783 \quad \quad \quad {}^1_0\text{neutron} \quad 1.00867$$

5. For the above, what is the binding energy in kJ/mol **nucleons**?

**Miscellaneous**

1. Fe-56 is the most stable of all nuclei, has the greatest binding energy per nucleon
2. In nuclear reactions, the great amounts of energy are provided by nuclear “binding energy” that is released

**Fig. 20.3**

3. Fission reactions (Section 20.6): large nuclei fragment into smaller nuclei
4. Fusion reactions (20.7): small nuclei combine to give bigger nuclei
5. Both fission and fusion occurs to draw nearer the maximum stability of Fe-56

**Rates of Radioactive Decay (21.10)**

A. Nuclear half-life: radioisotope decay with 1<sup>st</sup> order rate laws, have characteristic half-lives ( $t_{1/2}$ )

<u>Isotope</u>	<u>Half-Life</u>	<u>Notes</u>
${}^{238}_{92}\text{U}$	5 * 10 <sup>9</sup> years (5 billion years)	Slow enough so that plenty is still left from when earth was made
${}^{40}\text{K}$	1 * 10 <sup>9</sup> years (1 billion years)	<ul style="list-style-type: none"><li>• Daughter nucleus is <math>{}^{40}\text{Ar}</math>.</li><li>• Used to date old rocks. The ratio of <math>{}^{40}\text{Ar}</math> to <math>{}^{40}\text{K}</math> reflects how much time has passed.</li></ul>
${}^{14}\text{C}$	5730 years	Medium half life, used to measure the ages of artifacts used during human history
${}^{131}\text{I}$	8 days	Short, used in medical imaging
${}^{24}\text{Na}$	15 hours	Short, used in medical imaging
${}^{99}\text{Tc}$	6 hours	Short, used in medical imaging

Notes:

1. For radioactive nuclei to be around, they must either have:
  - a. Long half-lives so that there hasn't been enough time for the original stuff to decay away. ( ${}^{238}\text{U}$  and  ${}^{40}\text{K}$ )
  - b. Have some source by which they have been made more recently.
    - ${}^{14}\text{C}$  is continuously made in the atmosphere as result of cosmic rays acting on  ${}^{14}\text{N}$
    - Radioactive nuclei used in medical imaging techniques ( ${}^{131}\text{I}$ ,  ${}^{24}\text{Na}$ ,  ${}^{99}\text{Tc}$ ) must be made fresh by laboratory techniques.
2. Radioactive nuclei used in medical imaging techniques or in chemotherapy must have relatively short life times.
  - You want them radiating so the doctors can detect whether the solution is going where it should.
  - But once the analysis is completed, you'd like the body to be free from them as soon as possible. (Rather than irradiating your DNA for weeks for no reason.)

## B. Radioactive Decay Math

- Radioactive nuclei decay via first-order rate laws
- Formulas for First Order Reactions:  $kt = \ln ([A_o]/[A_t])$        $kt_{1/2} = 0.693$

$\ln (A_o/A_t) = 0.693 \cdot t / t_{1/2}$	When solving for the amount of material left after a given time, given the half life
$t = (t_{1/2}/0.693) \ln (A_o/A_t)$	When solving for time, given half life and quantities of material

$$t_{1/2} \cdot \ln (A_o/A_t) = 0.693 \cdot t$$

Rearranged version when solving for  $t_{1/2}$ 

- $A_o$  = original amount of material
- $A_t$  = amount after time t
  - Amounts can be in mass, or in emission rate, or activity, or 100%  $\rightarrow$  percent.
- $t_{1/2}$  = half life, the time for half of the material to decay
- Boxed formulas are the ones you'll be given on the test
- Handling "ln y = x" on calculator, when you know "x" but want to solve for "y": enter "x", then hit your "e<sup>x</sup>" button.

1.  $^{99}\text{Tc}$  is used for brain imaging scan. The half-life for  $^{99}\text{Tc}$  = 6.0 hours. What percentage of a dose of  $^{99}\text{Tc}$  is left after 24 hours?

2.  $^{131}\text{I}$  has a half-life = 8.0 days. How long will it take to decay for a sample to decay so that only 10% of the original  $^{131}\text{I}$  survives?

3.  $^{90}\text{Sr}$   $t_{1/2} = 28.8$  g If 42 g of  $^{90}\text{Sr}$  is buried, how much is left after 120 years?

## C. C-14 and Carbon Age Dating: Measurement of Human History Dates.

- carbon-14 is a very small, low abundance isotope of carbon. C-12 is the major isotope, C-13 next. But the C-14 is good for finding human history dates.
- $^{14}\text{C}$   $t_{1/2} = 5730$  years
- Since most of human history has been within the last few thousand years, the half-life for carbon-14 ends up being pretty appropriate.

The logic of Carbon dating:

1. A steady state percentage of  $\text{CO}_2$  in the air is radioactive  $^{14}\text{CO}_2$ .
  - a. The  $^{14}\text{CO}_2$  in the air is produced from  $^{14}\text{N}$  as the result of cosmic rays
  - b. Plants take in  $^{14}\text{CO}_2$  directly from the air via photosynthesis.
  - c. Animals and humans take in  $^{14}\text{C}$  indirectly, either by eating plants that have  $^{14}\text{C}$  or by eating animals that ate the plants with the  $^{14}\text{C}$ .
2. All living things (plant or animal) have a known steady state percentage of  $^{14}\text{C}$  relative to total carbon
  - This results in a known  $^{14}\text{C}$  radioactivity rate, relative to total carbon
  - $A_0$  is known
3. Once a living thing dies, it stops incorporating  $^{14}\text{C}$ .
  - Plants stop photosynthesizing, people and animals stop eating
4. After death, the radioactive  $^{14}\text{C}$  decays at  $t_{1/2}$  rate, and the  $^{14}\text{C}$  radioactivity rate declines, relative to total carbon
5. By looking at the  $^{14}\text{C}$  activity, you can determine approximately how long it's been since something that was formerly alive has died
  - Wood, cloth, anything ex-biological...
  - After a couple of half lives, the amount of  $^{14}\text{C}$  radiation gets too low to allow much accuracy

Problem.  $^{14}\text{C}$  has a half-life = 5730 years. "Live" carbon has activity of 15.3. A shirt is claimed to be Jesus's, but is found to have carbon activity of 14.0. How old is the shirt, and can the claim be true?

Rock dating similar:

- When lead is formed by sources other than  $^{238}\text{U}$  decay, isotopes other than just  $^{206}\text{Pb}$  are formed, so you can tell that the  $^{206}\text{Pb}$  came from the  $^{238}\text{U}$ .
- By measuring the ratio of  $^{40}\text{K}$  to  $(^{40}\text{K} + ^{40}\text{Ar})$ , or  $^{238}\text{U}$  to  $(^{238}\text{U} + ^{206}\text{Pb})$ , you can determine what fraction of the original  $^{40}\text{K}$  or  $^{238}\text{U}$  is left, figure out how many half-lives have passed, and figure out how long ago a rock formed.

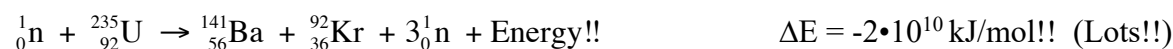
**Nuclear Fission**

Fig. 20.6

**Keys**

1. Fission: When a larger nucleus breaks to give smaller nuclei
2. Humongous energy release!!
3. Fact: neutron bombardment doesn't always result in the same fission. Sometimes the  ${}^{235}\text{U}$  fragments in other ways to produce other daughter nuclei. Fig. 20.7
4. Neutron: both a reactant and a product!!
  - more neutrons are produced than are absorbed!
5. Branching and the uranium fission "chain reaction" Fig. 20.7
  - more neutrons produced than absorbed  $\Rightarrow$  more neutrons can strike other uraniums and cause more fission reaction  $\Rightarrow$  more neutrons  $\Rightarrow$  more fissions (and energy), etc..
  - Proliferating neutrons  $\rightarrow$  proliferating fissions  $\rightarrow$  proliferating energy, proliferating chain reaction (and maybe a uranium fission bomb, WWII Japan...)
6. "Critical Mass": enough  ${}^{235}\text{U}$  is required to support chain
  - "subcritical"- There isn't a large enough block of  ${}^{235}\text{U}$  to absorb the neutrons. While a given fission may absorb only one neutron and produce several neutrons, most of those neutrons produced just escape, rather than hitting another  ${}^{235}\text{U}$ , causing another fission reaction, and propagating/proliferating the chain
  - "supercritical": more than enough  ${}^{235}\text{U}$  so that more than enough of the neutrons produced bump into another  ${}^{235}\text{U}$ , cause another fission, and propagate/proliferate the chain.
  - Nuclear fission bomb: 2 subcritical masses are smashed together to achieve supercritical mass. The chain reaction then propagates/proliferates!!
    - A chemical bomb is actually used to propels one mass into the other!

**Nuclear Reactors: Major Components**

1.  **${}^{235}\text{U}$  fuel rods** (last for years)
  - subcritical: can't explode
  - these are not pure natural uranium; rather they are enriched in  ${}^{235}\text{U}$
2. **Cadmium control rods** to control the rate of reaction and provide emergency security
  - a. The control rods are adjustable and are suspended in between the fuel rods
  - b. The control rods absorb neutrons.**
  - c. They can block the spray of neutrons from one fuel rod to another and prevent chain reaction.
  - d. The rate of chain reaction is controlled by raising the control rods just high enough so that enough neutrons can get through and sustain the chain reaction.
  - e. As a fuel rod ages and becomes less active, it needs more neutron hits to sustain the chain reaction, so the fuel rods get raised higher and higher.
  - f. Many automatic controls are in place to drop the control rods and stifle chain reaction in case of any emergency
3. **A coolant (water) absorbs energy**, produces steam that drives turbine  $\Rightarrow$  electricity

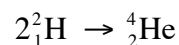
Concern: what do with spent fuel rods, still with some radioactive content?

- Current process: “vitrifications”
  - Fuel rods get “melted” and dissolved in liquid glass;
  - The liquid glass gets poured into a steel can, cools, and glasses over.
  - For one year plant: only one barrel gets produced!!

“Breeder Reactors”      $^{238}\text{U} + {}^1_0\text{n} \Rightarrow {}^{239}\text{Pu}$

- Active Plutonium is “bred” from relatively inactive  $^{238}\text{U}$  by bombardment with high-speed neutrons

### Nuclear Fusion



- Solar process, hydrogen and deuterium fusion is how the sun produces it’s energy!
- Ideal energy dream: no radioactive byproducts, huge energy, cheap  $\text{H}_2\text{O}$  provides lots of hydrogen (and a good amount of deuterium) for fuel!!
- Problem: huge temperatures are needed (to overcome nuclear repulsion) in order to push Hydrogens together in order for them to fuse
  - Materials that can contain and support such high temperatures are not currently practical
- Hydrogen-bomb (cold war, never used in actual wars): a uranium fission bomb is used to provide the heat needed to support fusion!

**Radiation: Effects and Units**

1. rad = energy absorbed/body mass (dosage) (1 food calorie = ½ million rads)
2. rem = biological damage  
effective dose = rads x impact factor  
(dose) (quality)

Key: “rems: measures risk  
 a) not all rays equal  
 b) dosage doesn't consider variance in penetration

Typical: < 0.4 rems/year (cosmic, x-rays, radon...)  
 > 25 rems to cause trace damage  
 > 500 rems → 50% chance of death within 30 years

**Rays and damage (depends on whether internal or external)**

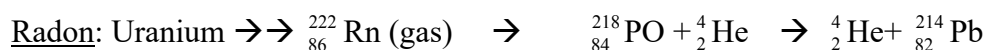
α: little penetration, only irritates outer skin (bad if generated internally)

β: penetrates a few mm

- γ While external α and β radiation does little serious harm because it never penetrates to vital organs, internal α and β radiation is much more harmful
- if the source of the radiation is inside the lungs or liver or kidney or brain, etc., large doses of these rays can be damaging even without penetrating far

γ: high energy, deep penetration, maximum damage

- γ radiation can generate DNA mutation
- γ radiation generated internally is actually not all that bad, because many of the γ rays largely escape!



1. Radioactive radon gas is produced from certain natural underground uranium sources
2. The radon gas seeps through basement cracks or into underground mines
3. Because the radon is heavy, it kind of sits in the basement, rather than just floating away
4. Because the radon is a gas, when you breathe the air you breathe some radon in, into your lungs
5. The radon is a major alpha emitter
6. From outside that wouldn't be much of a problem, but when you breathe it into your lungs and it's alpha-emitting in your lungs, the radiation can damage lung tissue ⇒ lung cancer.