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Chem 103 Lecture 9a

Admin:

Return: Test #2 88±27

(59% ±18)

A ≥ 120 ; B ≥ 105 ; C ≥ 70

Highest: 147/150 (98%)

Last time:

- 1) batteries
- 2) corrosion

Today: 1) electrolysis

2) Nuclear chem

Electrolysis:

b) Electrolysis cells (nonspontaneous)

Useful in electrolysis:

current and charge transferred:

Charge =  $q$  = #moles of electrons x charge of a mole of electron =  $nF$   $F=96500\text{Coul}$

If  $X$  moles of  $\text{Cu}^{2+} \rightarrow \text{Cu}$ , then  $q$  transf'd =

$(X \text{ moles of } \text{Cu}^{2+})(2 \text{ mol e/mol } \text{Cu}^{2+})(96,485 \text{ Coul})$

Current = flow of charge = coul/s =  $i$ .

So, charge =  $(i)(t)$  = coul.

Moles electrons transferred =  $it/F$

#mol substance =  $it/nF$  (where  $n$ =stoichiometric factor)

for example:  $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}$

check the oxidation numbers, we know then that:

$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$  (here  $n = 2$ )

And  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$  (here  $n=2$ )

Example:

$2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$  what is  $n$ =? (i.e #e<sup>-</sup> transferred)

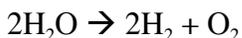
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eg. Water is hydrolyzed to oxygen and hydrogen gas.

- a) How many mLs of H<sub>2</sub> gas will be generated if water is hydrolyzed at 3.0 V for 2.0 hours at 1.80 amperes? (assume STP conditions)
- b) Write the half reactions
- c) determine the reaction in the anode.
- d) which half reaction will generate acidic conditions?

Solution:

Balanced equation:



so  $n = 4$ ,  $i = 1.80 \text{ A}$ ,  $t = 2.0 \times 60 \times 60 = 7200 \text{ sec}$   
 $\text{mol H}_2 = it/nF = (2.0)(7200)/(4)(96500)$   
 $= 0.0373 \text{ mol}$

$V = nRT/P = .0373(.0821)(273)/(1) = 0.836 \text{ L}$   
 $= 836 \text{ mL}$

### **nuclear chemistry:**

0) Nuclear chemistry: bridges chem & physics

-Diff from other areas of chemistry:  
chem rxns involve e's (moderate E's)  
nuke rxns involve nuclei (extremely high E)

-Involved modern technologies:  
power plants to wrist watches, & smoke detectors.

- controversial uses: nucl bombs, nucl. plants

1) Nuclear reactions: result of unstable nuclei.  
Spontaneous. Irreversible.

- called "nuclear *decay*"

- the unstable nuclei are called  
*radionuclides*

- nuclear rxns release radiation

- powerful forces involved and energies tremendous. so large they are described by  $E=mc^2$ .

- Referred to as "*ionizing radiation*" to differentiate from less energetic

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radiation (like light, IR and near UV)

2) Types of radiation, particles in nuclear decay:

Their symbols:

In general:  ${}_z^AX$  where:  $z$  = atomic #

=charge and

$A$ =atomic mass # = #protons(p)+#neutrons(n)

nuclear decay lead to release of

3 major kinds of radiation:

particle	symbol	charge	mass(amu)
alpha	${}_2^4\alpha, \alpha,$ ${}_2^4\text{He}$	+2	4
beta	${}_{-1}^0\beta, {}_{-1}^0e$	-1	0
gamma	${}_1^0\beta, {}_{-1}^0e$	-1	0

symbols of nuclear particles (*nucleons*):

neutron  ${}_0^1n$

proton  ${}_1^1p$

positron  ${}_{+1}^0\beta, {}_1^0e$

atomic mass #

symbol of a nucleus:  ${}_Z^AX$

where: atomic # (charge),

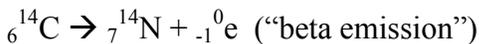
(3) Nuclear Decay : spontaneous breakdown of unstable nuclei

example:

${}_6^{12}\text{C}$  is "carbon -12" = it's the most common isotope of C

(it has 6 protons & 6 neutrons)

But there is also: Carbon-14: (it has 8 neutrons) Carbon-14 is unstable and undergoes decay:

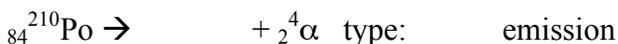
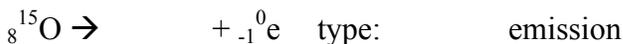


we can detect presence of C-14 from  $\beta$  emission.

(4) Balancing nuclear reactions:

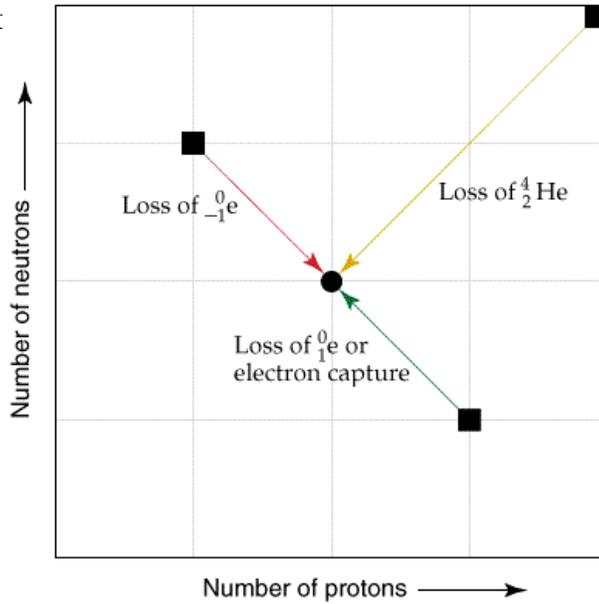
note how to balance nuclear equations: A and Z must balance. Write #'s for ease of balancing.

Example of nuclear reactions (fill in blanks):



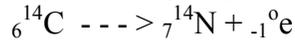


If above the belt:  $\beta$  emission to increase Z if below the belt: can do positron emission or electron capture

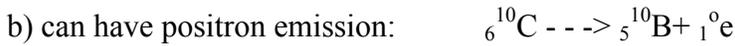
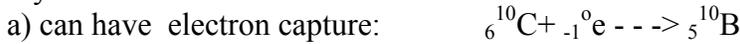


Understand the differences:

Say we have C-14: that's above the belt of stability. (beta emission):



say we have: C-10

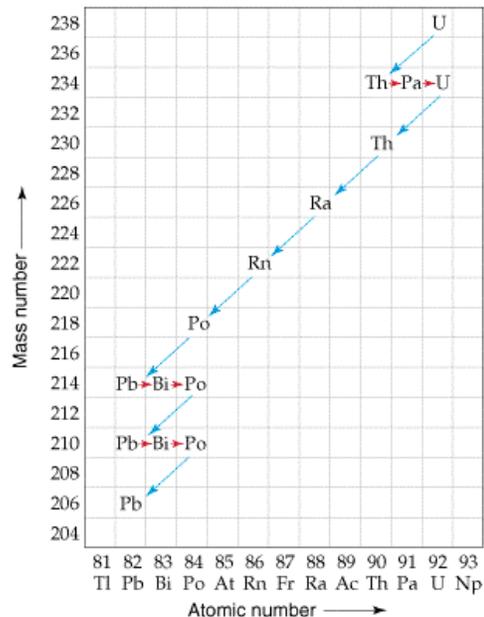


Note that elements above 80 tend to undergo alpha emission (both n and p decrease by 2)

(7) Radioactive series: Often, nucl. decay involves a *radioactive series*

For uranium, U-238: U-238  $\rightarrow$  Th-234  $\rightarrow$  U-234, e

(see below for the radioactive series for U-238)



(8) **Binding energy (BE):** a measure of the force holding the nucleons together in a nucleus:

consider:

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kJ/mol

1.007825 1.008665 2.01420 g/mol

**mass defect**,  $\Delta m$  = loss of mass (due to nonconservation of matter)

The missing mass is converted into energy by Einstein's equation:  $E = mc^2$

$\Delta m$  = products - reactants masses = 2.001410 - (2.00380) = -0.00239 g/mol

$\Delta E = (\Delta m)c^2 = (2.39 \times 10^{-6} \text{ kg/mol})$

$\times (3.00 \times 10^8 \text{ m}^2/\text{s}^2) =$

$= -2.15 \times 10^{11} \text{ J/mol}$

(9) **Binding energy (BE/n) per nucleon**: a measure of nuclear stability  
**Binding energy (BE)** = energy required to separate nucleus into its individual nucleons:

In the above case, BE per nucleon:

$2.15 \times 10^{11} \text{ J} / 2 = 1.08 \times 10^{11} \text{ J/nucleon}$

${}^4_2\text{He}$ : BE/n =  $6.84 \times 10^{11} \text{ J/nucleon}$  (more stable)

(10) All spontaneous nuclear reactions are **exothermic**.

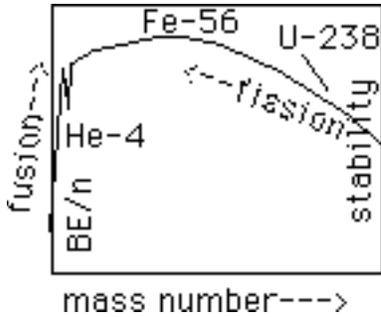
Note: all exothermic rxns (both nuclear and chemical) convert mass to energy but in chem rxns,  $\Delta m$ 's too small to detect and we say: *conservation of mass* holds.

BE per nucleon:  $2.15 \times 10^{11} \text{ J} / 2 = 1.08 \times 10^{11} \text{ J/mol n}$

for  ${}^4_2\text{He}$ : BE/n =  $6.84 \times 10^{11} \text{ J/mol n}$   
(more stable)

plot of BE/nucleon: shows that most stable are around Fe-56. (the greater the BE/nucleon, the greater the stability of the nucleus. That means all elements are thermodynamically unstable relative to Fe-56.

Heavier elements tend to break up into smaller nuclei by fission to come closer to Fe-56 while smaller nuclei tend to fuse (fusion) to form larger nuclei to be closer to Fe-56.



### 11) Rates of decay:

Radioactive decay is essentially **1st order**.

1st order rxns have a half life indep of starting amount: It is always the same no matter how long it's been sitting around...

$N \rightarrow$  products:

$$dN/dt = -kN$$

$$dN/N = -k dt$$

integrating both sides:

$$\ln(N/N_0) = -kt;$$

$$N = N_0 e^{-kt}$$

$$\text{If } t = t_{1/2} \quad N = .5N_0:$$

(by definition)  $t_{1/2} = \text{half life}$

$$\ln(.5) = -kt_{1/2}: -0.693 = -kt_{1/2}: k = (0.693)/t_{1/2}$$

$$\text{so } N = N_0 e^{-0.693t/t_{1/2}}$$

If  $t_{1/2} = 3$  yrs, how much will remain after 12 years? (ie  $12/3 = 4$  half lives)

$$N = N_0 (1/2)^4 = N_0/8$$

(N is meas'd indir as Curie (Ci). or in dpms.)

if  $N_0 = 12$  mCi at  $t=0$  and  $N = 8$  mCi at  $t=120$

days, what is  $t_{1/2}$ ?  $\ln(8/12) = -k(120) \Rightarrow$

$$.0405 = -120k$$

$$k = 3.38E-3: t_{1/2} = .693/3.3E-3 = 205 \text{ days. artificial}$$