An Overview of Nuclear Chemistry

 Many of you will have never seen anything about nuclear chemistry in your "pre" classes, yet will be expected to understand something about it in yourr "advanced" coursework or continuing education, e.g., WMD's, hence, an overview section is presented here.

The table, below, summarizes the salient features differentiating nuclear chemistry from "ordinary" chemistry.

Nuclear Chemistry	Ordinary Chemistry	
Elements are converted from one to another.	No new elements are produced.	
Particles within the nucleus are involved.	Usually only the outermost electrons are involved.	
Tremendous amounts of energy are released or absorbed.	Relatively small amounts of energy are released or absorbed.	
The rate of the reaction is NOT influenced by external factors.	The rate of the reaction is dependent upon factors like concentration, absolute temperature, catalyst, pressure, ad nauesum.	

Definitions

• Nuclear fission is defined as splitting a heavy nucleus into lighter nuclei.

 Nuclear fusion is defined as the combination of light nuclei to make a heavy nucleus.

Nuclear Fission

- Splitting a heavy nucleus into 2 or more lighter nuclei with the release of energy
- Fission PRODUCES more neutrons than it UTILIZES
- HENCE: Nuclear Chain Reaction occurs
- This liberates huge amounts of energy and can quickly get out of control without some kind of regulation
- Minimum mass required to support this selfsustaining chain reaction = CRITICAL MASS



Subcritical Mass

- Less than critical mass; most neutrons escape into surroundings without hitting a nucleus
- First A-bombs: subcritical mass wedges surrounded by IMplosives
- Drove wedges together to each critical mass
- Explosion: 0.01-0.02 megaton blast in 1945
- In 1995, add a few grams of tritium to improve efficiency of explosion: 60 megaton

(REFERENCE: ALL bombs exploded in WW II = 6 megatons)

Supercritical Mass

- More than the critical mass
- Most neutrons will hit nucleus
- If this happens to be ²³⁵U, will cause explosion

More Fission



²³⁵U is Rare – How Get Radioactive Material, Then?



Breeder Reactor!

- ²³⁹Pu = dangerous poison; dangerous carcinogen
- Inhalation of < 5 μg causes death
- Pu fuel is more concentrated than U fuel (safety problems with storage and transport)
- ²³⁹Pu used in A-bombs and other nuclear weapons have to have heavy security with this fuel

Fission Reactor

- Control Rods: made from neutron absorbing metals: Cd and B
 - Too few neutrons and reaction dies out
 - Too many neutrons and get overheating, core melted down and maybe thermonuclear explosion (SAFETY SYSTEMS!)
- Moderator: slows neutrons to most appropriate Energy for 235U fission initiation



Fission Rate Regulation

- Increase Fission Rate
- Raise control rods in core
- Decrease Fission Rate
- Lower control rods in core

When rods are full "IN" core, shuts down reactor.

Fuel Rods

• Are enriched from 0.7% to 3.0% used with water because increased numbers of neutrons combine with hydrogen instead of uranium:

$${}^{1}_{1}H + {}^{1}_{0}n \rightarrow {}^{2}_{1}H = \underline{D}$$

- D₂O is more efficient because neutrons do NOT combine well with deuterium.
- Therefore, D_2O reactor runs on the cheaper 0.7% fuel pellets (in the rods; UO_2)
- BUT, D costs money to make, hence 6 of one and a half dozen of the other.

FUSION

- Combination of light nuclides to form heavy nuclides are THERMONUCLEAR REACTIONS because they only occur at high temperature
- "Cold Fusion"
- FUSION REACTORS: best so far seems to be:

$${}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n + 17.6 MeV$$

- This reaction requires an energy of activation of 10 keV, but the energy obtained is 17.6 MeV!
- Fusion reaction products do NOT produce waste with long half lives.

PROBLEM

- T is very rare how make more?
- With Li
- Wrap D and T in a Li "blanket"

Li Blanket Tritium Production



- BIG Problem: the temperature required to run the D+T reaction in the Li blanket is 2*10⁸ K
- At this temperature, matter is present as PLASMA: gas made up of separated electrons and positively charged nuclei
- How do you confine this "plasma"?
- It vaporizes everything solid known to man!

Magnets Confine the Plasma

 This answer was reached in response to learning that magnetic fields are known to restrict motion of charged particles in space



Fusion

- Greatest success, though, so far, is the hydrogen bomb (H-bomb)
 – Lithium-6-deuteride: ⁶Li²H or ⁶LiD
- The energy from the fission portion of the 2-step reaction is in the form of γ emissions.
- This energy is used to "drive" the second reaction to completion.

Two Staged Reactions

Fission: ${}^{6}_{3}Li + {}^{1}_{0}n \rightarrow {}^{4}_{2}He + {}^{3}_{1}H + 4.8 MeV STEP 1$ Fusion: ${}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n + 17.6 MeV STEP 2$ ${}^{6}_{3}Li + {}^{2}_{1}H \rightarrow {}^{4}_{2}He + 22.4 MeV TOTAL$

Ionizing Radiation

- Ionizing radiation is defined as any type of radiation which has the energy to "bump" an orbital electron from the atom with which it is interacting.
- The remaining product (the cation and the ejected electron) is called an ion pair.



Ionizing Radiation

- Emissions with enough energy to ionize/fragment atomic particles along the path of the emissions;
- Hazardous to health because can cause damage to living cells and cause genetic defects, as well.
 - Hiroshima and Nagasaki
 - Chernobyl

Energy of Ionizing Radiation

- In units of MeV: megaelectron volt
- 1 eV = the energy acquired by an electron when it is accelerated by 1 volt
- $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} (1 \text{ J} = 1 \text{ Nm}^2/\text{kg}^2)$
- 1 J = 4.184 calories
- 1 amy = 932 MeV

RadioACTIVITY

- The number of atoms that disintegrate per unit time
- SI = Becquerel (Bq) = 1 disintegration per second (dps)
- OR
- Curie (Ci) = disintegration rate of 1 gram of Radium (3.7*10⁻¹⁰ dps)
- 1 Ci = 3.7*10⁻¹⁰ Bq



- In order to "be" a radioisotope, an element must be above or below a band of stability.
- This band of stability is shown, above. It is determined by plotting the number of neutrons in an element vs the number of protons in that same element.
- Note that the band of stability does NOT follow a one to one ratio, rather it is curvilinear, following the one to one (1:1) ratio at low molecular weights (these elements have the greatest stability).
- Once this region is passed, the curve begins to take on 1.2:1, 1.4:1 and 1.5:1 ratios.
- The region marked by the dashed lines above and beneath the band of stability (solid line), but NOT including the band, itself, is the region where radioactive nuclides occur.

Atomic Nomenclature of Nuclear Arrangements

Definitions and Terms

Arrangement	Atomic number	Atomic mass	Neutron number	Examples
Isotope	Same	Different	Different	Barium Nuclides
Isobar	Different	Same	Different	Iodine and Xenon
Isotone	Different	Different	Same	Iodine, Xenon and Cesium
Isomer	Same	Same	Same	Glucose and Galactose

Barium Nuclides -- Isotopes



Iodine and Xenon -- Isobars



Iodine, Xenon and Cesium --Isotones

Glucose and Galactose -- Isomers



Radionuclides/Radioisotopes: Nuclei that Decay Spontaneously



Decay Equations -- Particulates

Above the Band of Stability

•In this case, the number of neutrons is much greater than the number of protons so these nuclides want to lower their n/p ratio.

•There are two mechanisms by which they can do this: beta (β) decay or neutron emission.

• β -emission occurs when a neutron decomposes to a proton and an electron.

•Note the "old way" of showing this, as there are still those of us around who demonstrate it this way.

- <- oldway

- Examples of β -emission are illustrated below.
- Note that the top number is the atomic mass and the bottom number is the atomic number.
- Note also that the numbers all add up on both sides of the reaction (decay), hence, 228 radium 88 (Molecular Weight, Element, Atomic Number) decays to 228 actinium 89 and an electron.
- Likewise, 14 carbon 6 decays to 14 nitrogen 7 and an electron. 234 thorium 90 decays to 234 protactinium 91 and an electron.



Neutron Emission

- Although neutron emission is uncommon, there are some examples below.
- Note that 137 iodine 53 decomposes to 136 iodine 53 and a neutron. 17 nitrogen 7 decays to 16 nitrogen 7 and a neutron.



Decay Equations -- Particulates Below the Band of Stability

- •In this instance, the nuclides want to raise their n/p ratio.
- •They may do this via positron emission or by K electron capture.
- •It is of great importance to remember that the "K" referred to in the previous sentence is NOT a potassium ion, rather it is a K shell electron that will be captured.
Positron Emission

- In positron emission, a proton is decomposed to a neutron with a mass of 1 and a charge of zero and a positively charged electron (positron) of mass zero and a charge of +1.
- Examples of positron emission are shown right.
- Note that 39 potassium 19 decays to 38 Argon 18 and a positron.
- 15 oxygen 8 decays to 15 nitrogen 7 and a positron.
- 8 boron 5 decays to 8 beryllium 4 and a positron.



K Capture

- Examples of K capture are illustrated below.
- Note that 106 silver 47 captures an electron (K type) to form 106 palladium 46.
- 37 argon 18 captures an electron to form 37 chlorine 17.
- 7 beryllium 4 captures a K electron to form 7 lithium 3.

Some Radioisotopes Undergo Both Positron Emission and K Capture

- 3% of the time, 22 sodium 11 captures a K electron to form 22 neon 10.
- 97% of the time, 22 sodium 11 undergoes positron emission to form 22 neon 10.

"Na + _ip -> 22 Ne 22 Na -> 22 Ne + +1P

Below the Band of Stability or with Atomic Number > 82

- The particles emitted members of this group are helium atoms (4He2; read 4 helium 2) and the decay is called alpha (α) decay or emission. The emission of an α particle raises the n/p ratio, right.
- 204 lead 82 undergoes alpha decay to form 200 mercury 80 and a helium atom.
- 226 radium 88 undergoes alpha decay to form 222 radon 86 and a helium atom.
- 210 polonium 84 decays to 206 lead 82 and a helium atom.
- Note that the numbers add up, again, on both sides of the decay equation.
- 238 uranium 92 decays to 234 thorium 90 and a helium atom.

204Pb ->	200Hg + 2He
226 Ra ->	222 Rn + 2He 86 Rn + 2He
210 Po ->	206Pb + 4He 82Pb + 2He
238U ->	2347h + 2He

- Thus far we have looked at particulate forms of ionizing radiation.
- Remember from CHEM 121 that electromagnetic radiation has dualistic properties, i.e., it has both particulate properties and wave-form properties.
- The wave-form properties are the next area of study.

Decay Equations -- Wave-Form

Gamma (y) Radiation

- When a positron (anti-matter) collides with an electron (matter), the process is called annihilation and gamma rays are emitted. Positrons are short-lived as there are so many electrons present in nature. Gamma radiation is high-energy radiation.
- Remember back to CHEM 121 Planck's and Einstein's equations, below. Remember, too, that when these two equations are equated, that they tell us that mass may be converted to energy -- Hiroshima and Nagasaki are devastating reminders of this concept.

$$E = h n$$

$$F = mc^{2}$$

$$F = mc^{2}$$

$$h n = mc^{2}$$

$$h n = mc^{2}$$

$$h n = mc^{2}$$

- Let's take a look at Planck's equation, first.
- Max Planck observed a relationship between energy, the speed of light in a vacuum, the wavelength of light and a proportionality constant.
- The latter was named in his honor and is called Planck's constant.
- As you can see in this figure, energy is related to the frequency of the "light" through the speed of light (c) and its wavelength (l).
- While the values for c and Planck's constant (h) are shown in the graphic, you are not going to be held accountable for memorizing them.

E= hc = hos remember v= I c= 3.10° m/s h= 6.626.10-34 Js N= sec-1

- Planck's equation works for visible light and "invisible" light (ionizing radiation), as well.
- In this graphic, we are asked to determine the wavelength of light that gives off 5 Joules of energy.
- Note that when the numbers are crunched that the answer comes out in meters.
- For the most part, we prefer to work in units of nm, hence the answer is converted to nm from m.

$$E = hnr = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \cdot 10^{-34} \text{Tz})(3 \cdot 10^8 \text{m/s})}{5 \text{ Jz}}$$

$$\lambda = 3.9756 \cdot 10^{-26} \text{ m}$$

$$\lambda = (3.9756 \cdot 10^{-26} \text{ m})(\frac{1 \cdot 10^9 \text{ mm}}{\text{m}}) = 3.975 \cdot 10^{-17} \text{ mm}$$

- Another example follows to determine the wavelength of light:
- the energy given off by a beam of light is 9.035*10⁻¹⁹ Joules (J). What is the wavelength of the light? As you can see in the solution, the wavelength of light is 220 nm -- in the ultraviolet region of the spectrum.

$$E = hv = hc$$

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{(6.626 \cdot 10^{-34} \text{Js})(3 \cdot 10^8 \text{m/s})}{9.035 \cdot 10^{-19} \text{J}}$$

$$\lambda = 2.20 \cdot 10^{-7} \text{m}$$

$$(2.20 \cdot 10^{-7} \text{m})(\frac{1 \cdot 10^7 \text{mm}}{1 \text{m}}) = 220 \text{ mm}$$

 Let's combine Planck's and Einstein's equations so that we may ask: what is the mass equivalent of a 400 nm photon of light?



Note that the correct answer is 5.522 milli-atto-femto-grams, i.e., an incredibly small mass.

Energy Loss Mechanisms for Gamma Rays

The table, below, summarizes the three energy loss mechanisms with graphics following to illustrate these

concepts

Energy Loss Mechanisms for Gamma Rays			
Name	Definition		
Photoelectric Effect	Gamma energy is absorbed with an inner shell electron ejected.		
Compton Scattering	Alters the flight and energy of the gamma radiation with ejection of an outer shell electron.		
Pair Production	The loss of a whole nucleus with electron and positron pair produced.		

Photoelectric Effect



Gamma energy is absorbed with an inner shell electron ejected.

Compton Scattering



Alters the flight and energy of the gamma radiation with ejection of an outer shell electron.

Pair Production



The loss of a whole nucleus with electron and positron pair produced.

Gamma Radiation vs X-Radiation

- The putative sources of both of these sorts of ionizing radiation.
- It seems that the source of x-radiation is the electron cloud after excitation while the source of gamma radiation is from the nucleus of a radioactive atom.
- The former is commonly encountered via an electrical machine and the latter is spontaneously emitted.
- At this level the "only" difference is the SOURCE -- BUT! If their energies are identical, you can't tell them apart.

The Production of X-Radiation

- The general idea behind the production of x-rays for clinical applications.
- In general, an electron beam is bombarded from a source (a filament) against a rotating anode (the "whirring" sound you've heard when you get an x-ray).



- The electrons interact with the electron clouds (raising the electrons to a higher state, then relaxing them -- Figure at right -- blow up of electron clouds' energy levels) causing the x-rays to be "shot through" the patient onto x-ray film.
- Additionally, as the electrons relax, they give off infra-red energy -- heat!
- This is one reason why x-ray exam rooms are cold -- to preserve the rotating anode so it will last a long time (the oil in the head helps with this, too).
- The other reason has to do with the perceived fear of the "movement" of x-rays, i.e., in the early days, people were afraid that x-rays would travel throughout the building through the heating ducts and spread out over the building "twitching" everyone in it -- doesn't happen, yet still carries over as the lack of heating in many of these rooms even today.



- You may have noticed in many emergency rooms (although this is changing), operating rooms and dentists' offices that when you get x-rays taken that there is no "whirr" -- only a "click".
- This is because many use fixed anodes for these machines. A fixed anode does not rotate.
- When bombarded with projectile electrons, the fixed anode develops a "pit" at that site and burns out faster than a rotating anode which is hit in many different spots by electrons.
 - It is important to also keep in mind that when working with βemitters (electron emitters) that you do NOT want to protect yourself by placing lead shielding between you and it: x-rays will be formed!
 - Use layers of multi-density "plastics" that are available.

Radiation "Dosage"

- RAD = Radiation Absorbed Dose the amount of radiation that results in the absorption of 0.01 J/kg of irradiated material
- SI = Gray (Gy); 1 Gy = 100 RAD's
- **RBE** = Relative Biological Effectiveness
 - $-\alpha$, p⁺, ¹₀n = 10
 - $-\beta$, γ , x-rays = 1
 - MEANING: former has 10 times the effect of the latter
- REM: Radiation Equivalent for Man: Dose (REM) = RAD * RBE

USEPA Radiation Exposure Limits for Man

- Radiation Workers: 5 REM/year
- General Population: 0.5 REM/year
- Average Natural Exposure: 0.15 REM/year
- A SINGLE 500 REM dose will kill ½ of the exposed population within 30 days!

The Inverse Square Law

- This law says that the intensity of radiation decreases by the square of the distance moving away from the source.
- Conversely, it says that the intensity of radiation increases by the square of the distance moving towards the source.
- Figure below illustrates this arithmetic relationship.
- Note that "I" is intensity and "d" is distance; "1" and "2" are selfexplanatory.



- An example: the intensity of x-rays at 4 feet is 10 intensity units (we're not gonna get hung up on the correct units -- I want you to get the idea of this).
- What is the intensity at 16 feet?
- By crunching the numbers, we find that the answer is 0.625 intensity units.

 $\frac{1}{T} = \frac{\sigma_2}{12}$ $\frac{I_{1}J_{1}^{2}}{J_{1}^{2}} = I_{2}$ $T_{2} = \frac{(10)(4)^{2}}{(16)^{2}} = \frac{10(1)^{2}}{(4)} = \frac{0.625}{1 \text{ Intensity}}$ Units

- The reverse process, i.e., as we get closer to a source of radiation: the intensity of gamma rays at 8 feet is 8 intensity units.
- What is the intensity at 2 feet?
- The answer is 128 intensity units.

 $\left(\frac{d^2}{12}\right)$ $I_1\left(\frac{d_1^2}{d_2}\right) = I_2 = 8\left(\frac{8}{2}\right)^2 = 128$ Intensity Unil

Characteristics of Selected Radiations

We have examined the decay of nuclides in terms of chemistry. We have not examined them in terms of the ranges they will travel in two media: air and soft tissue. The table, below, does exactly that:

	Type of Radiation	Range	
		In Air	In Soft Tissue
α	Particulate	1-10 cm	0.1 mm
β		0-10m	0-2 cm
X	Wave-form	0-100 m	0-30 cm
γ		0-100 m	0-30 cm

- The clinical correlation to this is that α particles can be stopped with newspaper, β particles can be stopped with appropriate "plastic" shielding; X and γ rays will penetrate the body –
- Point:
 - 1) detrimentally, e.g., Hiroshima and Nagasaki and/or
 - 2) usefully as in x-rays of the body for diagnostic purposes.
- Keep in mind that as the patient becomes more and more obese that it becomes more and more difficult to obtain meaningful radiographs "on" these patients.
- Gamma radiation has been shown to be very safe in sterilizing foodstuffs for long term storage and to prevent infectious, fatal, bacteria from causing disease, e.g., E. coli strains (O157H7) that have caused JITB syndrome.
- The general public, though, remains uninformed and fears this technology -- much like the fear felt when MRI was called NMR imaging.
- Didn't change the technology, just changed the name and blitzed the public with a spin on the technique.

The Rate of Decay

- When working with radioactive compounds, it's always nice to know how long they'll "be around", e.g., ^{99m}Tc, thallium, radioactive iodine -- all used in clinical scenes for different scans.
- The decay of radioisotopes follows first-order kinetics:
- Note that
 - "In" stands for natural log;
 - "A_o" is the concentration of "A" (the radioactive substance) at time zero;
 - "A" is the concentration of "A" at time = "t";
 - "t" = that time;
 - "k" is the decay constant (a fudge factor that is different for every nuclide).

 $ln\left(\frac{A_{o}}{A}\right) = kt$

- Part of understanding the arithmetic behind the decay of nuclides is determining the half-life of the substance.
- The half-life (t_{1/2}) is the time it takes for 50% of your sample to decay.

A= 0.5 Ao=1 ln (Ao) = k t 1/2 tyz= half life $ln(\frac{1}{0.5}) = k t'/2$ en 2 = k + 1/2 0,693 ln 2

Half-Life

 Half life is NOT effected by chemical combination or by temperature or pressure changes

- The application of these two equations follows on the next slide (half-life determination [one may also obtain the rate (decay) constant from this equation, as well] and first-order kinetics, respectively) in example form:
 - If the half life for 90 strontium 38 is 28 years and you have a 0.5 g sample, how much 90 strontium 38 was present 14 years ago?
- Note that the original sample (calculated) had an activity mass of 0.7072 g.
- For perspective, consider that a good portion of the radioactive waste that is being proposed to be stored in southern Nevada has a half life on the order of several billion years.
- Not a problem in our life-time -- for future generations, though, consider the possibilities and draw your own conclusions.

1)
$$t_{1/2} = \frac{\ln 2}{k}$$

 $k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{28 \text{ yrs}} = 0.62475 \text{ yr}^{-1}$
2) $\ln \left(\frac{A_0}{A}\right) = kt$
 $\ln A_0 - \ln A = kt$
 $\ln A_0 - \ln A = kt$
 $\ln A_0 = kt + \ln A$
 $= (0.02475)(14) + \ln 0.5$
 $= 0.3465 + (-0.693)$
 $\ln A_0 = -0.3465$
 $A_0 = -0.3465$
 $A_0 = -0.3465$
 $A_0 = -0.3465$

- The application of the first order equation on chemical reactions follows, as well, for the decomposition of C to D and E:
 - if half of C is used up in 60 seconds, calculate the fraction of C used up after 10 minutes.
- As you can see on the following slide, 99.9022% of the C is used up.

$$c \rightarrow D + E$$

$$t_{1/2} = \frac{2n^2}{k}$$

$$k = \frac{0.693}{60} = 0.01155 \text{ s}^{-1}$$

$$l_n(\frac{C_0}{C}) = k + C_0 = 1 \text{ (C_0} + \frac{1}{2} \text{ (C_0} + \frac{1}{2}$$
Radiodating

- Isotopic applications may also be used to determine the age of different objects, e.g., bones, wood, stored nuclear waste.
- Examples follow.

- You found a piece of wood near Washoe Lake that was determined to have 0.45 the activity of wood cut today.
- The half-life of carbon-14 is 5730 years.
- How old is the wood?

$$t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730 \text{ yrs}} = 1.21 \cdot 10^{-4} \text{ yrs}^{-1}$$

$$2n \left(\frac{A_0}{A}\right) = kt \qquad \underline{A = 0.45A_0}$$

$$ln \left(\frac{A_0}{0.45A_0}\right) = kt$$

$$ln \left(\frac{1}{0.45}\right) = kt$$

$$0.7985 = (1.21 \cdot 10^{-4})t$$

$$t = \frac{0.7985}{1.21 \cdot 10^{-4}} = 6599.244 \text{ yrs}$$

- A bone found near Mt. Rose peak was determined to have 0.96 the activity of bones obtained today from the butcher.
- The half-life of 90 strontium 38 is 28 years.
- How old is the bone?

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{28} = 0.02475 \text{ yrs}^{-1}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{28} = 0.02475 \text{ yrs}^{-1}$$

$$k = \frac{1.65 \text{ yrs}}{0.02475}$$

- You have received a shipment 238 uranium 92 (half-life = 4.5*10⁹ years) to store.
- If you received 5 g today -- assuming 100% activity -how long would you have to store it until the sample had an activity mass of 0.25 g?



- Carbon-14 is present at about 1.1*10⁻¹³ mol% naturally in living matter.
- A bone dug up showed 9*10⁻¹⁵ mol % carbon-14.
- The half-life for carbon-14 is 5720 years.
- How old is the bone?

