## Today's info

- Exams were excellent as usual-"Everyone could almost do everything."
- Answer key will be distributed shortly
- Final is in two weeks!
  - assume 1/3 from each of the two exams and the remainder from the material after the second exam
  - have all of your tables
- If we reach at least 13 quizzes (likely), low three scores will be dropped
- The always popular final grade projector will be available soon.

#### Organic Chemistry Summary

- Be able to:
- name the basic compounds discussed
- sketch structures of simple hydrocarbons
- recognize the basic functional groups
- complete simple reactions such as oxidation of alcohols
- identify and name simple aromatic compounds including knowing the common names of those noted in class
- differentiate between basic types of isomersim and recognize the possibility of optical isomerism
- discuss simple polymerization processes

#### Isomerism

- *Different* compounds with the same formula are called isomers.
- What do we mean by different?
- The difference arises from variations in how the atoms are attached to each other. The variations can be in bond types or distributions.
- **Bonding isomers** will vary in the distribution of bonds among the atoms. These will have the greatest variations in properties.
- **Geometric isomers** vary in the 3-D distributions of the atoms in space. The simplest case is variation about a double bond



• **Optical isomerism** results from the mirror images being nonsuperimposable. This, usually, requires a carbon atom with **4 different groups** attached to it which is called the chiral center



#### Polymers

- *Polymer* means many parts and one commonly describes the component of a polymer as a *monomer*
- The polymer field is an extremely rich and practical aspect of organic chemistry
- Addition polymers-the monomer units are added successively to an ever growing chain-most "vinyl polymers"(PVC,polystyrene are made this way)
  - $n H_2C=CH_2$  (ethylene)=>( $CH_2CH_2$ )<sub>n</sub> (polyethylene)
  - n  $F_2C=CF_2$  (tetrafluoroethylene)=>( $CF_2CF_2$ )<sub>n</sub> (poly tetrafluoroethylene, aka TEFLON)
    - Chance favors the prepared mind
    - Enter "serendipity and science" in a search engine or, better yet, read this book: **Serendipity: Accidental Discoveries in Science** by Royston Roberts.
- **Condensation polymers**-the monomer units combine with the production of a product molecule (water or similar) as waste
  - polyesters logical result of a dialcohol reacting with a diester
  - polyamide diamine + a diester => nylon
  - or 2 aminoacids => proteins

#### Starch vs cellulose

• Starch



• Cellulose



#### Nuclear Stuff

- nucleus-protons and neutrons, then quarks then .. and then..
- everything may well end up as "strings"
- nuclei are built up starting with hydrogen with very large nuclei requiring several star generations
- Stability of a nucleus is best presented as binding energy per nucleon:



#### Structure of the nucleus

• It should not be surprising that it is felt that the nucleus has a quantized structure similar in principle to the quantized electronic structure



## Nuclear Stability-some facts

- There are nearly 300 stable nuclei known
- Over ½ have even numbers of neutrons and protons(eveneven)
- Of the remainder, nearly half are odd-even and the other half are even-odd
- There are almost no odd-odd nuclei
- This can't be accidental. The explanation is that "like" pairs increase stability of the nucleus
- neutrons/protons=1 early in the periodic table and then gradually increases
- A nucleus(isotope) which has too many neutrons will undergo a decay process that decreases the ratio while a nucleus which is neutron poor will undergo a decay process that increases the ratio

### Nuclear Decay

- Depending on the structure, certain nuclei are unstable. The simple explanation for this is that the "breakdown" of the nucleus leads to one which is more stable. Though a bit of a stretch, you could consider this analogous to why certain atoms readily form cations or anions, while others remain neutral.
- Be able to:
  - Understand the difference between  $\alpha$ , $\beta$ , and  $\gamma$  radiation
  - Complete reactions for  $\alpha, \beta^+$  and  $\beta^-$  decays
  - Complete basic fission reactions where a single nucleus breaks down into only two nuclei.
- There are three primary modes of nuclear decay
- $\alpha$  decay-loss of a helium nucleus with an accompanying decrease in the mass and atomic numbers
  - ${}^{M}X_{N} = {}^{4}He_{2}^{2+} + {}^{M-4}X_{N-2}^{-2}$
  - The emitted particle doesn't have enough energy to have escaped the nucleus?
- β
- $\beta$  electron emission-conversion of a neutron into a proton-increase in the atomic number  ${}^{M}X_{N} => \beta - + {}^{M}X_{N+1}$
- $\beta$ + positron emission-conversion of a proton into a neutron-decrease in the atomic number  ${}^{M}X_{N} => \beta$ + +  ${}^{M}X_{N-}$
- fission-breakdown of the nucleus into smaller nuclei. A material which undergoes such a process spontaneously is termed fissile. Of primary current interest are U<sup>235</sup> and Pu<sup>239.</sup> In balancing these, total mass and proton total must be conserved. Below is a generic example, not intended to indicate a real process

$${}^{178}A_{72} \Longrightarrow {}^{142}B_{52} + {}^{36}C_{20}$$

#### The chain reaction

• If the nuclear decay process produces neutrons, it is possible for then neutrons to strike another nucleus causing it to undergo fission early and produce more neutrons and so on. Reactions typical of uranium 235

$$U^{235} + n = = Ba^{144} + Kr^{90} + 2n$$
$$U^{235} + n = Ba^{141} + Kr^{92} + 3n$$
$$U^{235} + n = Zr^{94} + La^{139} + 3n$$

- The key to "managing" a chain reaction is control of the velocity and concentration of the neutrons(neutron flux).
- **critical mass** is the minimum amount which will sustain a chain reactiondepends on the purity. Critical mass for weapons is far less than that for reactor grade.
- One kilogram of Pu-239 being slowly consumed over three years in a conventional nuclear reactor can produce sufficient heat to generate nearly 10 million kilowatt-hours of electricity sufficient to meet the needs of over 1000 typical households. US currently has at least 5000 times that amount on hand with the technical ability to make an "infinite amount".
- The future-fission reactors or ethanol from corn?
- **Recommended reading:**The Making of the Atomic Bomb by Richard Rhodes (or go see "Fatman And Little Boy")

#### Transition Metal Complexes

- Recall basic tenets of Lewis Acid Base Theory
- A metal with a vacancy in a d level in any of its oxidation states is called a "transition metal"
- Recall that when metals in the transition series form ions, they never have s electrons
- Metal cations are Lewis .....
- L=ligand which will be a Lewis base
- $M^{x+} + nL => ML_n^{x+}$  transition metal ligand complex
- What makes these interesting:
  - they tend to be colored and considerable color variation is seen dependent on the metal, the oxidation state and the ligand
  - there is considerable variation in the electronic state of the complexes, including many which have multiple unpaired electrons.
  - variable valence and differing structures (octahedral, tetrahedral, and square planar) are seen
  - Given the nature of the possible ligands as well as other factors, metal ligand complexes are often quite labile. That is, ligands are added/removed/replaced relatively easily
  - The "traditional" bonding approach (Lewis Octet Theory), does not readily explain the observed properties of these materials.

## Valence Bond Theory

- VBT descriptions of TM complexes are relatively straightforward, but one must keep in mind that they are not predictive, but rather constructed based upon known properties of the complex (its structure, magnetism, etc)
- In constructing the description there are two primary issues
  - The metal cation is stripped of its valence s electrons. It is of primary importance that the metal electron count be properly determined.
  - The ligand and metal electrons do not "mix" as the ligand is bringing in electron pairs in the formation of the Lewis acid-base adduct
- There are 14 orbitals available to the metal d s p d

d	S	р	d

# Example

- A Co<sup>2+</sup> complex is octahedral and has 3 unpaired electrons-what is its VBT description
- Co <sup>2+</sup> is d<sup>7</sup>
- The metal electrons are placed in the d orbitals in accordance with the stated spin information
- $\underline{\uparrow \downarrow} \underline{\uparrow \downarrow} \underline{\uparrow} \underline{\uparrow} \underline{\uparrow} \underline{\uparrow} \underline{\uparrow} \underline{\uparrow} \underline{\uparrow}$
- Next, the six electrons pairs from the ligands are added

metal ligands the complex is described as high spin, outer sphere,  $sp^3d^2$ 

- An Fe<sup>2+</sup> complex is octahedral and has no unpaired electrons-what is its VBT description
- Fe<sup>2+</sup> is d<sup>6</sup>
- The metal electrons are placed in the d orbitals in accordance with the stated spin information

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- $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$
- Next, the six electrons pairs from the ligands are added

metal ligands the complex is described as low spin, inner sphere, d<sup>2</sup>sp<sup>3</sup>

- An Ni<sup>2+</sup> complex is tetrahedral and has 2 unpaired electrons-what is its VBT description
- Ni <sup>2+</sup> is d<sup>8</sup>
- The metal electrons are placed in the d orbitals in accordance with the stated spin information

  - Next, the four electrons pairs from the ligands are added

metal ligands

the complex is described as high spin,  $sp^3$ 

- An Ni<sup>2+</sup> complex is square planar and has no unpaired electrons-what is its VBT description
- Ni <sup>2+</sup> is d<sup>8</sup>
- The metal electrons are placed in the d orbitals in accordance with the stated spin information

  - Next, the four electrons pairs from the ligands are added
  - $\underbrace{\uparrow \downarrow} \Uparrow \downarrow \amalg \downarrow$

metal ligands

the complex is described as low spin, dsp<sup>2</sup>

Since it seems to work well, what's wrong with VBT?