Chem 130, Eppley
Fall 2017

KEY

Exam 3
Monday, Nov 20

1. (24 pt) For each of the following statements, justify using the information you've learned from this class. **Illustrate your answers with chemical equations and/or diagrams- a picture is frequently worth a thousand words!** (8 pt each)

   a. Metals conduct more at low temperatures but semiconductors actually conduct more at higher temperatures. A pure semiconductor is not as conductive as either a p- or n-type semiconductor.

Metals conduct better at low temp because there are fewer vibrations to prevent free movement of e⁻ in the solid (vibrations increase at higher temperatures). Semi conductors conduct more at higher temps because there is more energy for e⁻ to overcome the band gap and get into the conduction band. In p- and n-type the extra energy levels make the band gap smaller and easier to jump.

   b. A solution of NaF conducts electricity but solid NaF is non-conductive. The solid NaF is also brittle and has a higher boiling point than the similarly structured NaCl.

When NaF (an ionic solid) dissolves in H_2O, the ions move freely and can conduct electricity, however in the solid state the ions are locked in place and the ions cannot move. NaF is brittle because when the layers of solid are displaced, the like charges next to one another repel and cause the solid to break apart. NaF has a higher bp than NaCl because in $LE \propto -M\frac{Z_A Z_B e^2}{d}$, the d is smaller because F^- is in a lower quantum level than Cl^- so stronger interactions.

$Na^+ F^- Na^+ F^-$
$F^- Na^+ F^- Na^+$
$Na^+ F^- Na^+ F^-$
↓ ↓
$Na^+ F^-$
$F^- Na^+ \} Na^+ F^-$ ← repulsions
$F^- \} F^-$

   c. O_2 is paramagnetic and has a bond order of 2, but Li_2 (perhaps the "dilithium" of Star Trek fame!) is diamagnetic and has a very long and very weak bond (hence its instability and ability to power starships in fiction).

O_2:
— σ^*_{2p}
↑ ↑ π^*_{2p}
↑↓ ↑↓ π_{2p}
↑↓ σ_{2p}
↑↓ σ^*_{2s}
↑↓ σ_{2s}

Li_2:
— σ^*_{2p}
— — π^*_{2p}
— σ_{2p}
— — π_{2p}
— σ^*_{2s}
↑↓ σ_{2s}

The bond order in dilithium is lower and so it will have a longer bond.

O_2 paramagnetic: $B.O. = \frac{8-4}{2} = 2$

Li_2 diamagnetic: $B.O. = \frac{2-0}{2} = 1$ → longer weaker bond

2. (27 pt) For each of the following statements, fill in the blank with an appropriate answer: (3 pts each)

Xe a. An example of an atomic solid

PO_4^{3-} b. The conjugate base of HPO_4^-

acid w/ $pK_a < 7.19$ c. Example of a weak acid that can successfully protonate HPO_4^- $pK_a(H_2PO_4^-) = 7.19$

n-type d. The type of doping that adding As to pure Si will lead to

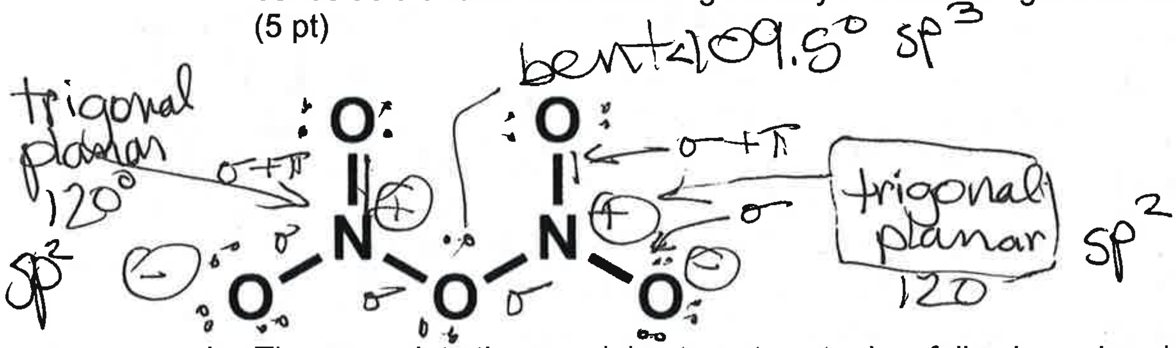
sp^3d^2 e. The hybridization of the central atom in XeF_4

intermetallic cmpd. f. The type of alloy where the structure is different than either of the original metals

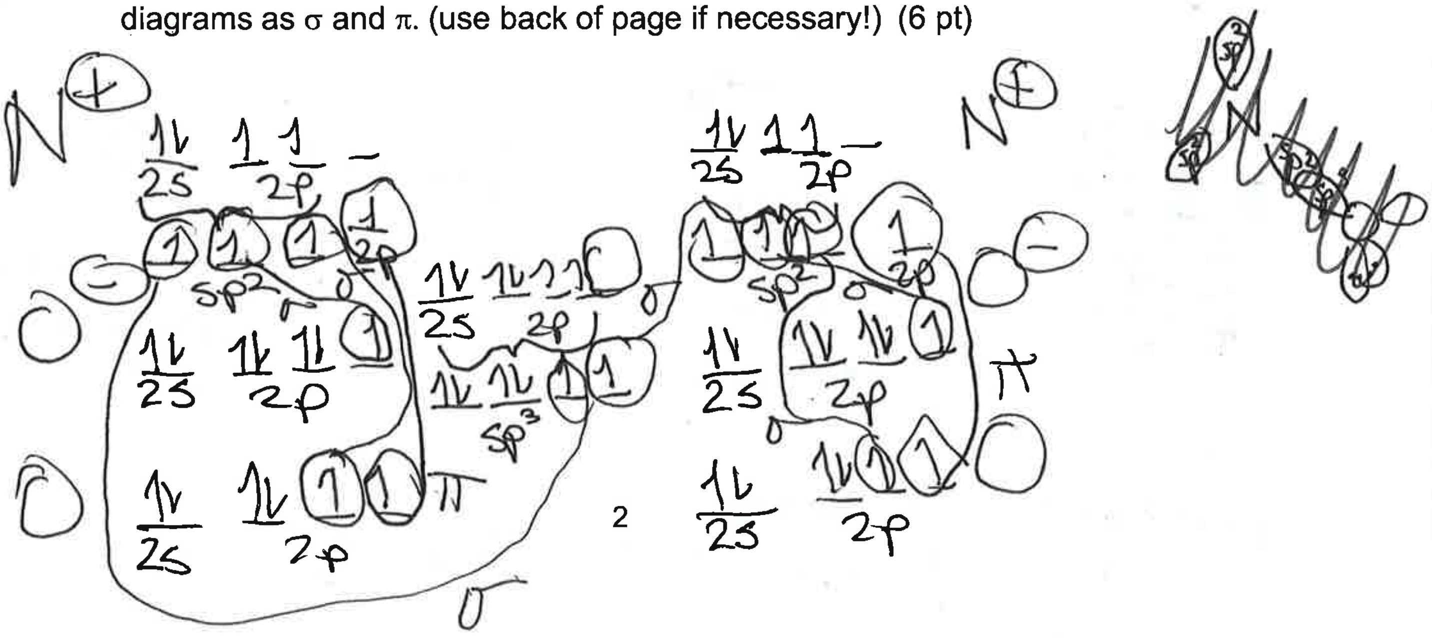
Na^+ g. A metal ion that is non-acidic

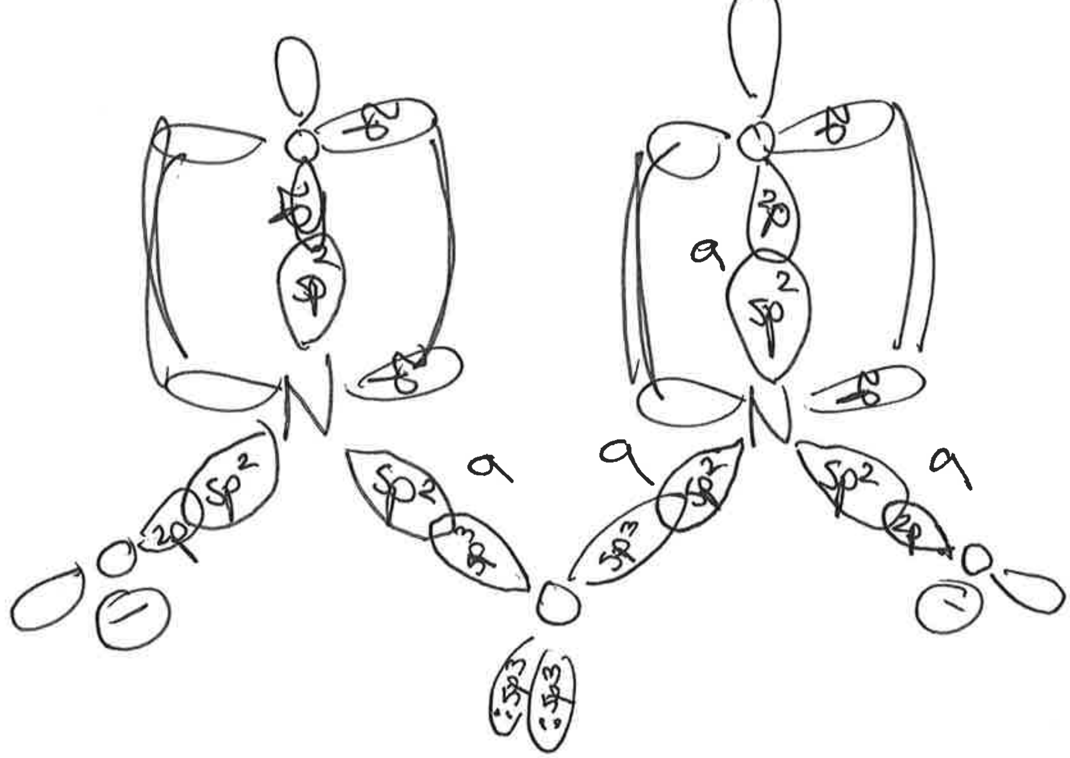
h. The shape of a σ_{2s}^* orbital in a diatomic MO theory description

3. (11 pt) The skeleton structure for N_2O_5 is shown below.
   a. Complete a valid Lewis dot structure for it and label any formal charges, label all bonds as σ and π. Indicate the geometry and bond angles of all central atoms. (5 pt)



   b. Then complete the remaining two steps to do a full valence bond description of the molecule, including the picture of the orbitals. Label bonds on both diagrams as σ and π. (use back of page if necessary!) (6 pt)

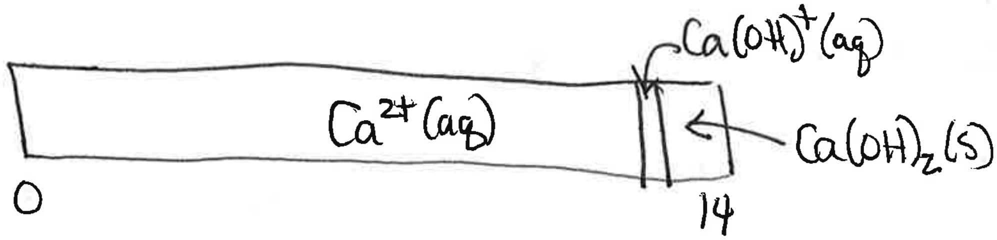



2p
sp2
2p
sp2
sp2
σ
σ
2p
sp2
σ
sp3
sp3
sp2
sp3
sp2
σ
2p
sp3
sp3

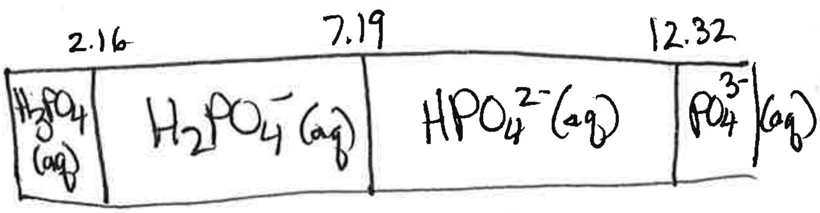
4. (12 pt) About 5 years ago Pepsi Co. successfully defended a $50000 lawsuit by an Illinois man who claimed to have found a dead mouse in his can of Mountain Dew. The company brought in a scientist who testified that no mouse could have remained recognizable in the can of soda after being in the can for 74 days (time was based on the can's production date), Let's consider this particularly gruesome statement for a minute. In particular the scientists attested that the pH of the Mountain Dew (3.4) would have affected the $Ca_3(PO_4)_2$ in the bones of the mouse. Consider the two ions that make up the $Ca_3(PO_4)_2$ in bone at that pH.

a. Draw **two separate** acid-base predominance diagrams (in the pH range of 0-14) for the two components of bone (Ca^{2+} and PO_4^{3-}). (6 pt)

Ca^{2+}



PO_4^{3-}



b. What forms of **each** of the two ions above are most important at the pH of 3.4 in the Mountain Dew can? (4 pt)

Ca^{2+} (aq)

$H_2PO_4^-$ (aq)

c. Briefly relate this information back to the case of the mouse in the Mountain Dew can. Note that $Ca_3(PO_4)_2$ is normally an insoluble solid. (2 pt)

The bones would react with the acid and the PO_4^{3-} would be protonated and become $H_2PO_4^-$ - Phosphates (like bone) are insoluble in water but $H_2PO_4^-$ salts are not!

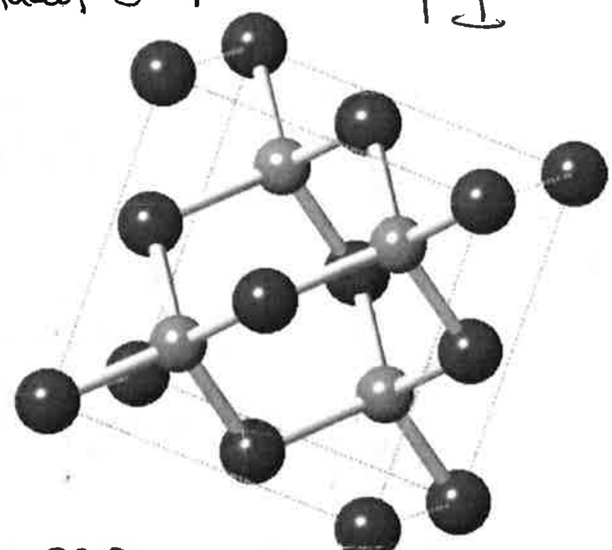
Surprise!: A mouse wouldn't stay whole for long in a soda can.
Credit: Wikimedia Commons/Shutterstock/C&EN

5. (19 pt) Below is a representation of a unit cell of an iodide of a particular transition metal ion. Try to figure out as much as possible using the figure on your test and then use the figure projected from the computer if necessary.

   a. The dark gray atoms are the transition metal ions and the light gray atoms are the iodide (these are gray and purple, respectively on the computer model). Using the symbol T to indicate the transition metal, write the formula for the solid based on the structure. **Show your work clearly** (5 pt).

   T 8x 1/8(corners) = 1 + 6x1/2(faces) = 3 = 4   TI

   I 4x1(full atoms) = 4



   b. What is the coordination number of the iodide? (2pt) 4

   c. What is the coordination number of the transition metal ion? (2 pt)

   4

   d. The transition metal ions form what kind of lattice in this structure? Is this closest packed? (4 pt)

   fcc yes fcc = ccp

   e. What type of holes do the iodides occupy? (2 pt) tetrahedral

   f. What percentage of those holes are occupied? (2 pt)

   50%

   g. At least one of the structures that you've encountered in the lab had an identical arrangement of atoms to this structure (the whole thing: cations + anions). Which one? (2 pt) zinc blende (or diamond)

6. (6 pt, 3 pt each) Rank each of the following groups as specified.

   a. Rank the following in order of increasing pK_b

   14-2.16 <0 9.25 ~~4.75~~ pK_b = 14-9.21 = 4.79

   $H_2PO_4^-$ OH^- AcO^- CN^- $OH^- < CN^- < OAc^- < H_2PO_4^-$

   11.84

   c. Rank the following solids in order of increasing boiling point

   Kr (atomic) Sc (metallic +3) Ca (metallic +2) K (metallic +1)

   Kr << K < Ca < Sc