Eppley, Chem 130

KEY

Exam 2
Friday, March 24
100 pts

1. (24 pt) Explain each of the following true statements, supporting your answers with diagrams and other supporting information as necessary! Note that it is better to say why your model does not fit the rather than just making up invalid stuff in order to make it agree! (8 pt each)

   a. The element gadolinium (Gd) tends to form +3 ions while the element indium (In) tends to form both +1 and +3 ions.

Gd $[Xe]6s^2 5d^1 4f^7$
Gd^{3+} $[Xe]4f^7$

In $[Kr]5s^2 4d^{10} 5p^1$
In^+ $[Kr]5s^2 4d^{10}$ ← remove 5p
In^{3+} $[Kr]$

For Gd, we remove the outermost n=6 e⁻ and the highest ℓ level n=5 e⁻ (5d) to form a +3 ion.

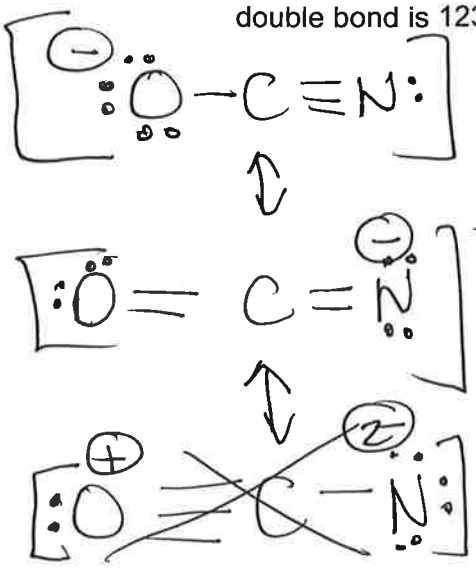
For In, we remove the 5p (highest ℓ in n=5) or the 5s and the 5p e⁻ (all highest n level) to form +1 and +3 respectively.

   b. Silicon (Si) and germanium (Ge) atoms are about the same size, but tin (Sn) atoms are bigger than both Si and Ge.

Si n=3
Ge n=4
Sn n=5

Sn is bigger than Si and Ge because it has e⁻ in a higher quantum level (n=5) than the other two. Si and Ge are about the same size b/c although Ge has e⁻ in a higher quantum level, it also has a higher Z_{eff} than Si, cancelling the effect of the higher quantum level.

   c. The CO bond length in the cyanate ion (OCN^- connected in that order) is 137 pm, while the average bond distance for a CO single bond is 143 pm, the average CO double bond is 123 pm and an average CO triple bond is 113 pm.

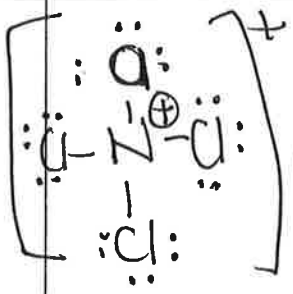
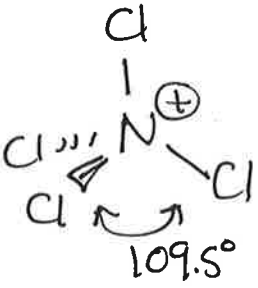
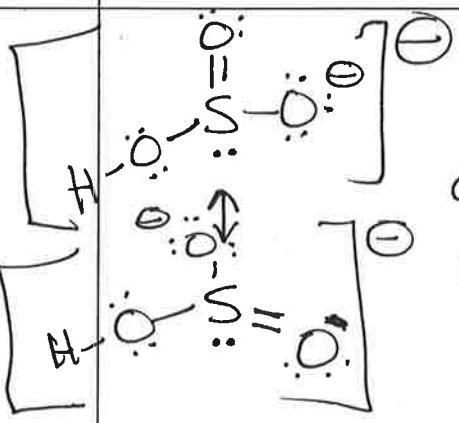
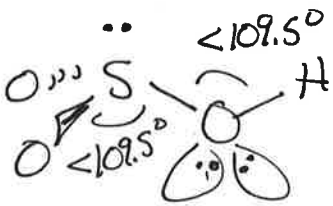
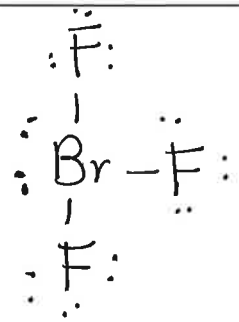
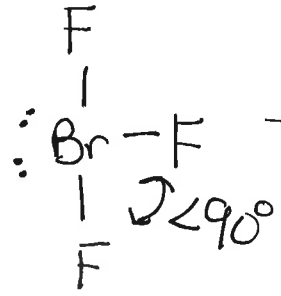


best structure

not important

The structures at the top is the best of the three resonance structures that can be drawn for OCN^- b/c it puts the formal neg charge on the most electronegative element (O). Because of that, the top structure will contribute most to the overall structure leading to a bond length for C-O that is closer to a single bond than a double bond.

2. (24 pts) Draw the **best** inequivalent Lewis dot structures (with equivalent resonance structures if appropriate) for the following molecules and ions. Predict the geometry, draw it in 3-D, label the bond angles. (8 pts each)

Formula	Lewis dot structure(s)	Draw geometry and indicate bond angles	Molecular geometry at **each** central atom(s)	Hybridiz. at **each** central atoms	Polar or non polar
NCl_4^+			tetrahedral	sp^3	non-polar
HSO_3^-			S = trigonal pyramidal O = bent	$S = sp^3$ $O = sp^3$	polar
BrF_3			T-shaped	sp^3d	polar

3. (8 pt) For each of the following statements say whether they are true or false. If false, explain why they are false, if true provide brief supporting evidence! (4 pt each)

False The Z_{eff} of Zn is higher than the Z_{eff} of Co because Zn has more d electrons.

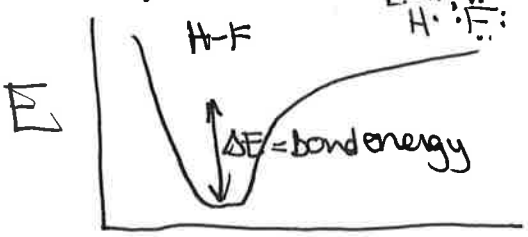
Explanation: Zeff of Zn is higher than that of Co because it has more pt than Co!

False XeF_4 is non-polar because the dipole moments of its lone pairs cancel out.

Explanation: XeF_4 is non polar b/c the dipole moments of the Xe-F bond cancel (lone pairs don't have dipole moments)

4. (7 pt total) A hydrogen atom and a fluorine atom are brought together from a significant distance apart to form a covalent bond. Draw a diagram that represents the **energy** associated with this system of two atoms as a function of the distance between them. Briefly explain the reasons for the energy changes that you plot on the diagram. On this diagram, indicate (with an arrow) the energy involved in breaking the HF bond.

   Would breaking this bond require the input of energy or would energy be released? Explain briefly the reason for the sign of this energy difference.



As you bring the two atoms together, the electrons in the bond will now be more stable because they are attracted to two nuclei rather than just one. It takes energy (+ΔE) to break the bond. Energy of the system goes up as the nuclei get super close together bc of repulsions of core e⁻ and nuclei of the two atoms

5. (12 pt, 3 pt each) Answer each of the following questions:

Kr a. The symbol for the element in period 4 with the highest Z_{eff}

Li b. The largest element in period 2

S→O c. A properly drawn dipole arrow for a O–S bond

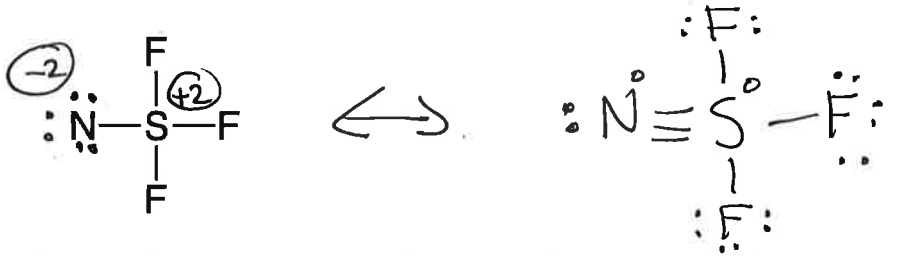
[Ar]3d⁸ d. The electron configuration of Ni^{2+}

(remove 4s)

6. (24 pt total) The simple bonding models that you've learned in this class can even be useful to describe the most exciting, novel inorganic compounds. In 2007, a paper (*Inorg. Chem.* **2007**, *46*, 1369-1378.) showed that $[XeF]^+[AsF_6]^-$ reacted with liquid NSF_3 to form the salt $[F_3SNXeF]^+[AsF_6]^-$. Those are some bizarre compounds! Let's look at some of the individual pieces:

For the starting material NSF_3, the skeleton structure is shown below.

a. Fill in the missing electrons and make a valid Lewis dot structure out of it. (2 pt)
b. Assign the formal charges to the initial structure you drew, and adjust the structure if necessary to give the best inequivalent resonance structure! (5 pt)



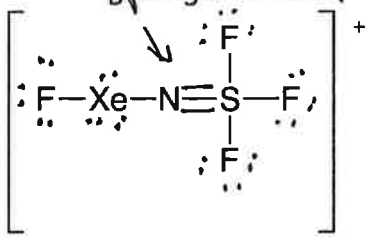
best structure b/c ∅ formal charge on S and N

For the novel product, there are two separate pieces which interact though ionic bonding: the AsF_6^- anion and the very interesting $[F_3SNXeF]^+$ cation.

The skeleton structure of the $[F_3SNXeF]^+$ cation is shown below (with no geometry implied). The paper states that it is the first example of a Xe bound to an "**sp hybridized N**".

c. Using the skeleton structure below, your answer to part b, and the important hybridization information above, propose a valid Lewis dot structure for this novel inorganic cation! (4pt)

sp hybridized



total e^- = 46
−12
34

d. Predict the following bond angles in the molecule based on your picture above (3 pt):

F-Xe-N 180° (linear based on 5 ED)

Xe-N-S 180° (linear based on 2 ED)

F-S-F 109°5 (tetrahedral based on 4 ED)

e. What experimental technique do you think the authors used to verify their bonding model for this cation? What information would you want to collect to verify your proposed bonding model. (3 pt)

X-ray crystallography – get actual bond distances and angles

f. The anion of the compound is a covalently bonded and much simpler anion, AsF_6^-. Do a full valence bond description of this anion (using all three steps that we did in class!). Start with a properly labeled Lewis dot structure! Clearly indicate the hybridization of the As in your answer and the orbitals used to form each of the bonds. Finally draw a picture showing those orbitals in the proper geometry. (8 pt)