

Name Solutions

You must attempt all ten questions on the exam. The value of each question is indicated. All submitted work must be your own effort. The Honor Principle applies to your submission of this exam. The last page contains equations and other potentially useful information. Feel free to tear it off to use during the exam.

1. (8 points) By our simple rules, the effective nuclear charge for the 2s and the 2p electron in boron should be equivalent. In reality, Z_{eff} for the 2s electron is slightly greater. Why? The 2p electron is more shielded because the 2s electron has a significant probability of being quite close to the nucleus. The 1s electrons are less effective, because of their penetration, in shielding the 2s electron.

(7 points) Which should have the greater effective nuclear charge, the 2p electron in oxygen or the 2p electron in neon? Why?



By our rules, only the 1s electrons shield the 2p electrons. So the crude calculation gives

$$Z_{\text{eff}}(\text{Ne}) \approx 10 - 2 = 8 \quad Z_{\text{eff}}(\text{O}) \approx 8 - 2 = 6$$

Neon has the greater Z_{eff}

2. (11 points) One of the excited states of H has the electron in the 4p orbital. List all possible sets of quantum numbers, n , l , and m_l , for the electron.

$$n = 4$$

$$l = 1$$

$$m_l = -1, 0, 1$$

$$m_s \text{ (not required)} = \pm \frac{1}{2}$$

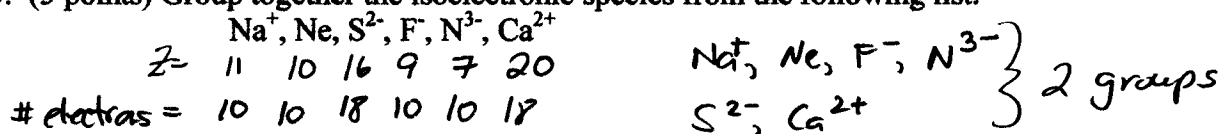
(4 points) How many nodal surfaces are associated with each one of the following orbitals? 2s 5d 5f

2s has 1 radial & 0 angular = 1

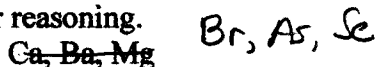
5d has 2 radial & 2 angular = 4

5f has 1 radial + 3 angular = 4

3. (5 points) Group together the isoelectronic species from the following list.

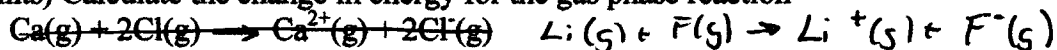


- (10 points) Arrange these elements in order of increasing ~~ionization energy~~ atomic radius. Briefly, explain your reasoning.

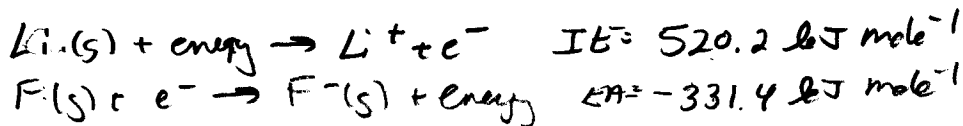


effective nuclear charge increased from As to Br
 Since the "binding energy" of the electron follows
 Coulomb's Law, $V = \frac{g_1 g_2}{r}$ where $g_1 = Z_{eff}$ the electron
 in Br is held more tightly and the radius is smaller.

4. (12 points) Calculate the change in energy for the gas phase reaction



Look at the partial reactions



$$\Delta H = 188.8 \text{ kJ mole}^{-1}$$

5. (10 points) Predict the relative bond energies for the series of molecules: HBr, HCl, HF. How did you arrive at your answer?

$$EN: F \quad (1681 + 331)/2 = 2012/2 = 1006 \text{ kJ mole}^{-1}$$

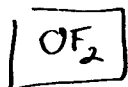
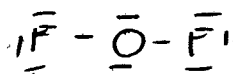
$$Cl \quad (1251 + 352)/2 = 1603/2 = 802 \text{ kJ mole}^{-1}$$

$$Br \quad (1139 + 328)/2 = 1467/2 = 734 \text{ kJ mole}^{-1}$$

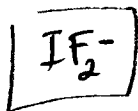
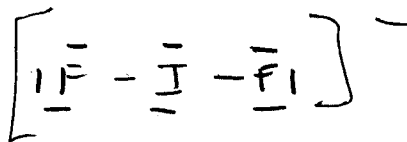
By EN Differences (greater difference = stronger bond)



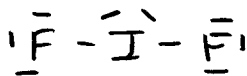
6. (24 points) For each of the following, provide a Lewis dot structure, the ideal geometry and the actual geometry. OF_2 , IF_2^- , ICl_4^- , ClO_3^-


 $20e^-$


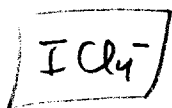
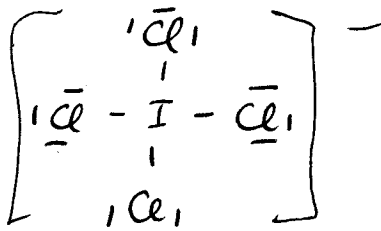
ideal = tetrahedral
actual = bent


 $22e^-$


need 2 more e^-



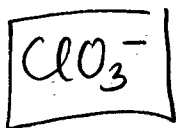
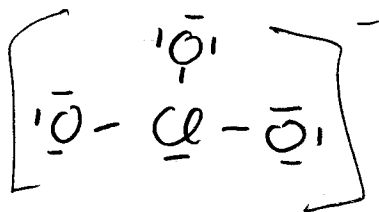
ideal = trig. bipyramidal
actual = linear (non bonding electrons are equatorial)


 $36e^-$


need 4 more e^-

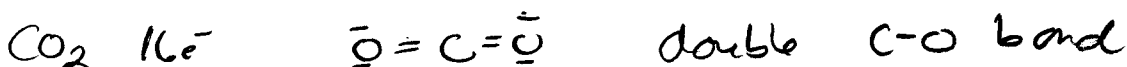
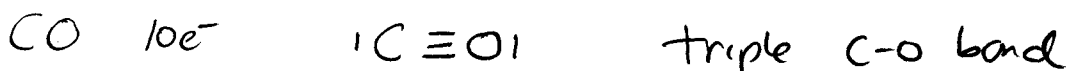


ideal = octahedral
actual = square planar
(non bonding e^- are axial)


 $26e^-$


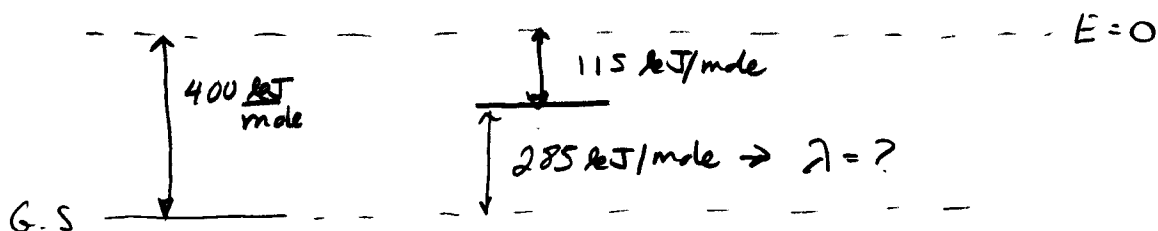
ideal = tetrahedral
actual = pyramidal
(like ammonia)

7. (10 points) The bond energy of one of the bonds in CO_2 is 532 kJ mol^{-1} , while the bond energy for CO is 1077 kJ mol^{-1} . Provide an explanation for this difference.



higher bond energy in CO is because a triple bond requires more energy to break than a double bond.

8. (20 points) The ionization energy of a certain element is 400 kJ mol^{-1} . When the atom is in its first excited state, the ionization energy is 115 kJ mol^{-1} . What is the wavelength of radiation emitted in a transition from the first excited state to the ground state?



$$E = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{E} = \frac{(6.62 \times 10^{-34} \text{ J}\cdot\text{s})(3 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{E}$$

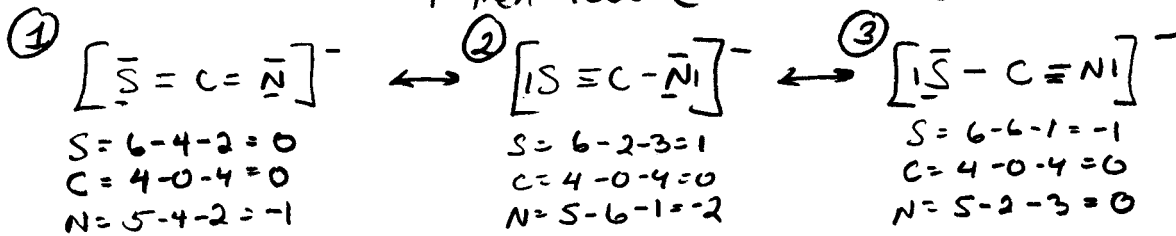
$$E \text{ per atom} = \frac{285000 \text{ J/mole}}{6.02 \times 10^{23} \text{ atoms/mole}} = 4.73 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{(6.62 \times 10^{-34})(3 \times 10^8)}{4.73 \times 10^{-19}} = 4.19 \times 10^{-7} \text{ m} = 419 \text{ nm}$$

9. (20 points) The thiocyanate ion, SCN^- , has three resonance structures (atoms are connected as shown...both the sulfur and the nitrogen are bound to the central carbon atom). Draw them and rank them in relative order of importance in terms of their contribution of their contribution to the observed structure of this ion. Describe the lengths of the carbon-sulfur and carbon-nitrogen bonds.

There are 16 electrons for a structure of the form S-C-N

$|\bar{\text{S}}-\bar{\text{C}}-\bar{\text{N}}|$ trial structure has $20e^-$; need 2 more bonds
+ then look @ formal charge



charge of -1 on N
N is more EN than
S, so this is very
favorable

charge of -2
on N - not
favored

charge of -1 on S
This is favorable, but
not as much as ①

$1 > 3 > 2$

expect that the C-S bond is between single + double, but
closer to double

expect that the C-N bond is between double + triple

but closer to double
[Because EN_N is close to EN_S, I accepted $3 > 1 > 2$ as well] \Rightarrow C-S bond close to single
C-N bond close to triple

10. (5 points) The lattice energies of KBr and CsCl are nearly identical. What can you conclude from this observation?

Sum of the radii of K and Br atoms is
approximately the same as the sum of the
radii of Cs and Cl.

(5 points) The lattice energy of MgO is approximately four times larger than that of NaF. Account for this observation.

charge on Mg is +2 while that on Na is +1
(and correspondingly for O and F)

$V \propto \frac{q_1 q_2}{r}$ for MgO $\rightarrow \frac{2e \cdot 2e}{r}$ for NaF $\rightarrow \frac{e \cdot e}{r}$ $\left. \vphantom{\frac{2e \cdot 2e}{r}} \right\}$ factor of 4
difference
(approximately)