

Spectrophotometry HW Questions:

1a. Briefly describe the process of Spectrophotometry.

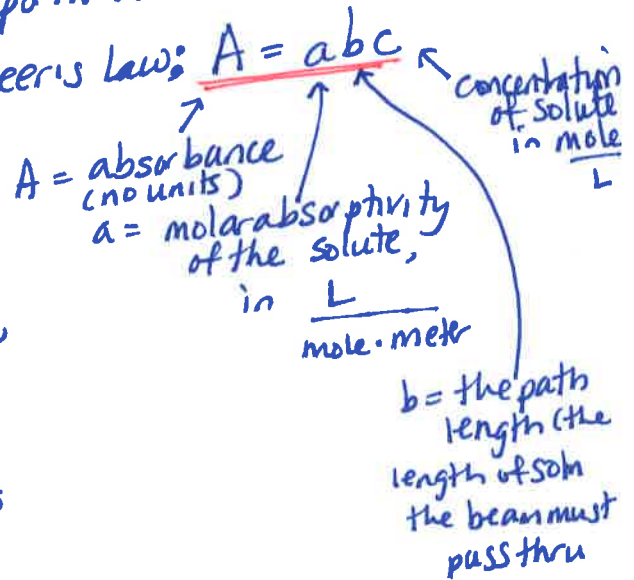
What does the machine do to the sample/what does it measure?

State Beer's Law, and explain what each letter stands for, and the units for each.

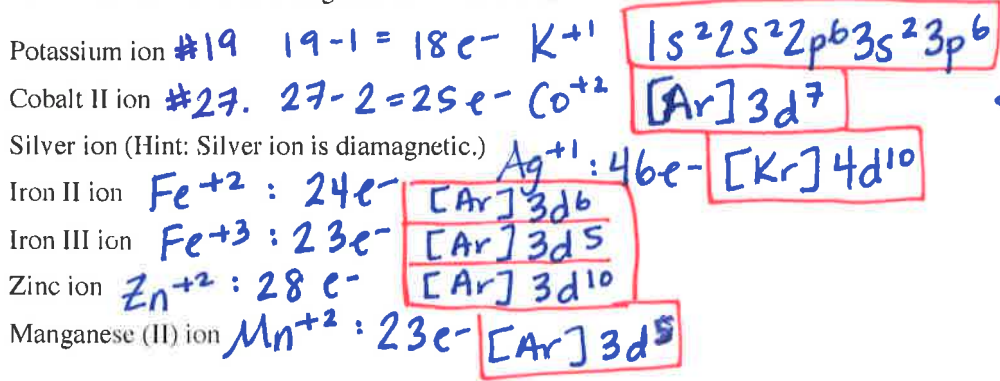
The spectrophotometer sends a beam of EM radiation through a liquid solution in a glass cuvette (a cuvette is essentially a test tube with a specific glass composition and test tube wall thickness). The machine measures the amount of light that is/was able to go through the sample and reach a detector on the other side of the sample. The transmittance is equal to the fraction of photons that make it from the source to the detector. For example, if 80% of the photons make it through the cuvette and sample, $T = 0.80$. The absorbance is calculated from the transmittance:

$A = -\log(T)$, so, for example, if $T = 0.80$, $A = -\log(0.80)$ so $A = 0.097$. Absorbance is proportional to the concentration of solute in the solution; acc to Beer's law: $A = abc$

so if you can measure the absorbance of a few samples with known concentration, you can solve for "ab" for the solute, (or for a and b individually), and then use the absorbance to find ion concentrations in solutions of unknown molarity.



1b. Write the electron configuration for each ion:



← (remember that transition metals lose their outer s electrons first when they form ions)

1c. Which of the above ions would you expect to have color vs which would you expect to be colorless? Explain.

Co^{2+} , Fe^{2+} , Fe^{3+} , and Mn^{2+} would be colored, since they have partially filled d-orbitals, and therefore would absorb visible light.
 Ag^+ , K^+ , and Zn^{2+} would be colorless since they have completely filled or completely empty d-orbital sublevels.

Cobalt (III) ion can form a complex ion using ammonia and chloride ligands.

d. Write the formula for the tetraamminedichlorocobalt III complex ion, including the charge. $[Co(NH_3)_4Cl_2]^+$

This ion has an octahedral geometry, with two possible geometric forms (or two "geometric isomers"). If the chlorides are next to each other (at 90°), the ion is called "cis-tetraamminedichlorocobalt III", and if the chlorides are across from each other (at 180°), it is called "trans-tetraamminedichlorocobalt III".

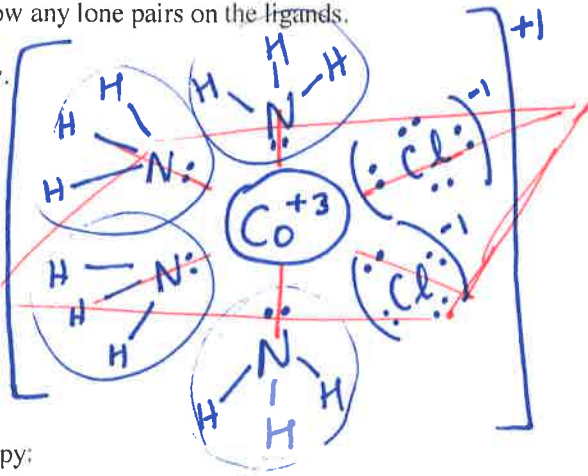
e. Draw a picture showing "cis-tetraamminedichlorocobalt III" ion. Show any lone pairs on the ligands.

f. The "cis" version of the ion absorbs yellow visible light most strongly. What would be the apparent color of a solution containing this ion?

violet, (the complementary color of yellow)

g. The "trans" version of the ion absorbs red visible light most strongly. What would be the apparent color of a solution containing this ion?

green (the complementary color of red)



PESPS (PhotoElectron Spectroscopy Problems!)

2a. Briefly describe the process that occurs in PhotoElectron Spectroscopy:

- What happens in a given atom?
- How are electron speeds measured?
- What does the kinetic energy of the electron tell us/how is it used in calculations – show the equation.

Photons of light (usually uv, but sometimes X-ray) are fired at a stream of atoms. When a given atom absorbs a photon, one electron is knocked off (of "ejected from") the atom, creating a +1 ion. The kinetic energy of the ejected electron is determined by measuring the radius of curvature as the e^- is deflected in a circular path by a magnetic field.

The Kinetic energy (KE) of the ejected e^- can be used to calculate the potential energy that was required to remove/reject the e^- from the atom (sometimes called the "electron binding energy") according to the equation: Binding energy = energy of the photon - Kinetic energy

$$BE = E_{\text{photon}} - KE = h\nu - KE$$

The B.E. is analogous to the "work function" with photoelectric effect, except that the sample is a beam of atoms instead of a solid sheet of metal.

← or "IE₁"

b. How does the data obtained using PES compare to an atom's "first ionization energy."
(how is it similar, and how is it different?)

Both the "Binding Energy" found with PES and the "first ionization energy" represent the energy required to remove one electron from a gas phase atom:



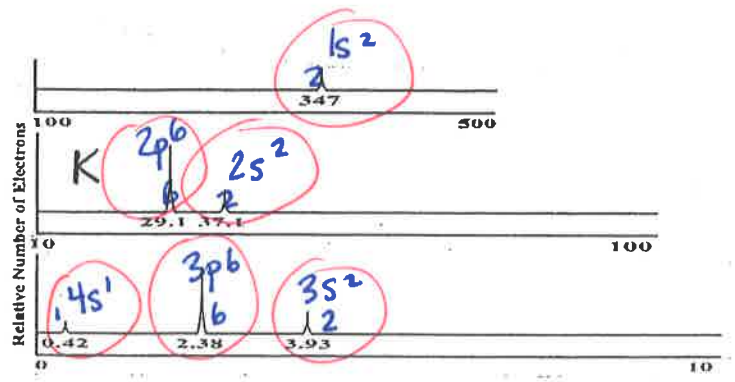
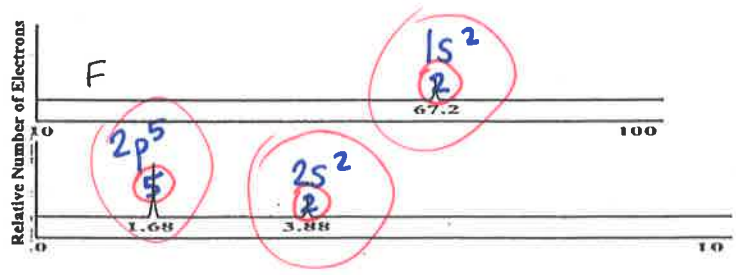
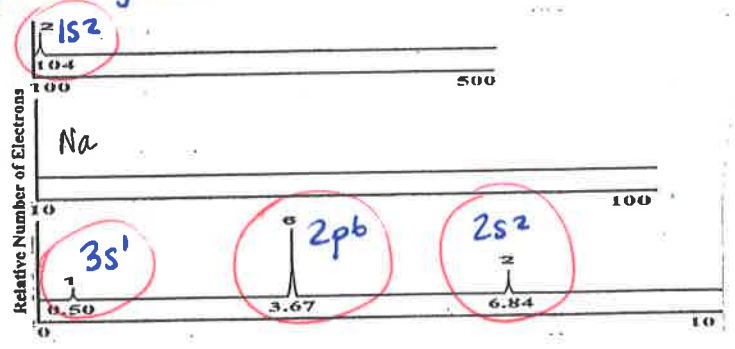
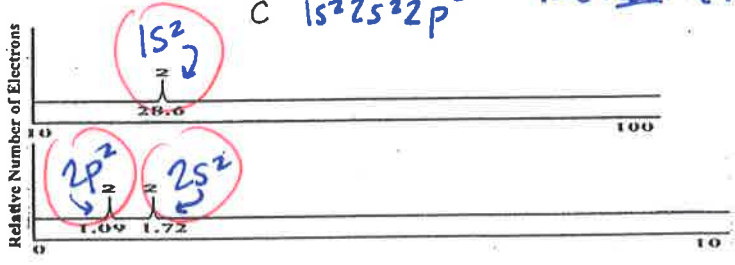
However, the IE₁ is the minimum energy required to remove an electron; IE₁ is the energy needed to remove the atom's highest energy electron. In PES, any one of the atom's electrons could be ejected, so the binding energies can be determined for an electron in any orbital, not just the highest energy orbital.

For example, Chlorine has the e- configuration 1s²2s²2p⁶3s²3p⁵. The IE₁ is the energy required for the 3p electron to be ejected, since 3p is the highest energy orbital type occupied. With PES, you would be able to determine not only the energy needed to eject a 3p electron, but you could also find the energy needed to eject a 3s, 2p, 2s, or 1s electron.

3. Consider the PES spectra for carbon, fluorine, sodium, and potassium, below.
(For each graph, the x axis represents "Electron Binding Energies in MJ/mole")

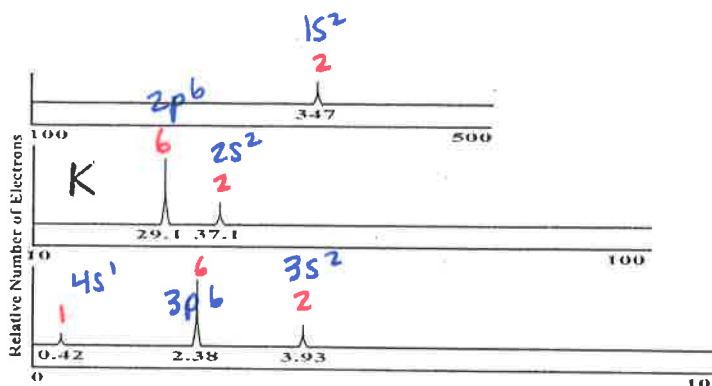
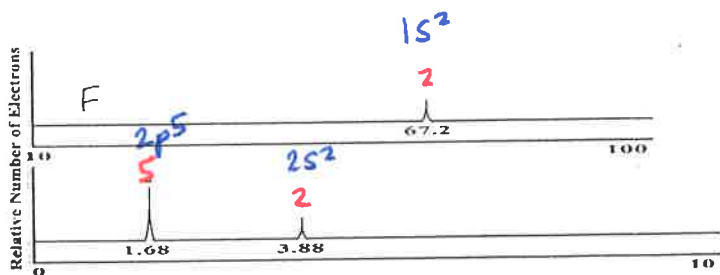
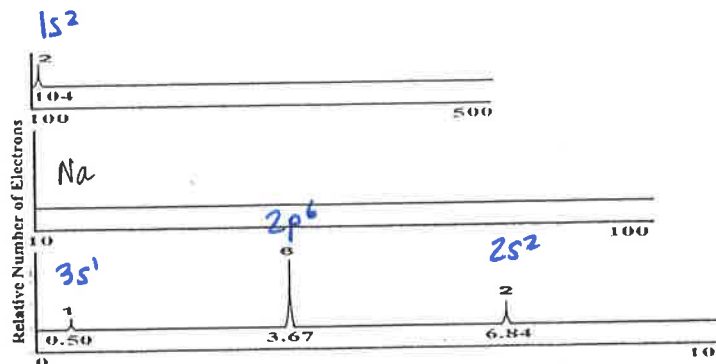
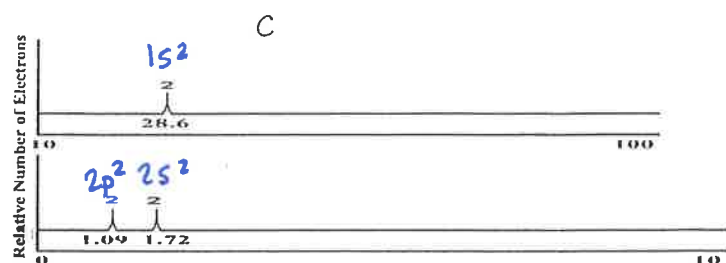
- a. For fluorine and potassium, write the relative peak height above each peak.
b. For all four spectra, write the corresponding part of the electron configuration (for example, "2p²") near each peak.

lowest E electrons - these will require the most E to leave
highest energy electrons, so these would require the least energy to be ejected



3. Consider the PES spectra for carbon, fluorine, sodium, and potassium, below. For each graph, the x axis represents "Electron Binding Energies in MJ/mole")

- a. For fluorine and potassium, write the relative peak height above each peak.
 b. For all four spectra, write the corresponding part of the electron configuration (for example, "2p²") near each peak.

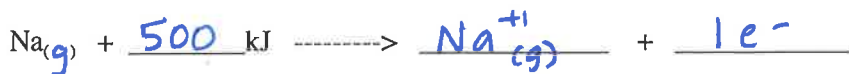


c. Use the graphs given above to find the "first ionization energy" of each element. (Hint: Should IE₁ correspond to the lowest or the highest energy required to remove the first electron?)

IE₁ of carbon = 1090 kJ/mole IE₁ of sodium = 500 kJ/mole (5.0 × 10²)

IE₁ of fluorine = 1680 kJ/mole IE₁ of potassium = 420 kJ/mole

d. For sodium, write a chemical equation, with phase subscripts, showing the process in the atom that corresponds to IE₁. Include the heat term in the equation. The equation is started for you:



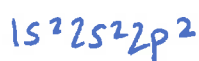
e. Why is the binding energy (B.E.) of the 1s electron SOOOO much larger than other binding energies? Use potassium as an example: Why is potassium's 1s B.E. so much larger than the 4s B.E.? Give 2 reasons.

- ① potassium's "1s" electrons ~~is~~ ^{are} much closer to the nucleus than its "4s" electron, so the "1s" electrons are more strongly attracted to the nucleus, and will therefore need more energy to leave.
- ② potassium's 4s electron only "experiences" an effective nuclear charge of about +1, since the +19 charge of the nucleus is shielded by the 18 core electrons. But the 1s electrons aren't shielded from the nucleus because no e⁻ are between 1s electrons and the nucleus. So the 1s electrons experience a nuclear charge of +19! So they're much more attracted to the nucleus, and need more energy to leave.

- f. What is the binding energy for sodium's 1s electron? 104 MJ/mole (104000 kJ/mole)
 What is the binding energy for potassium's 1s electron? 347 MJ/mole (347000 kJ/mole)
 Account for the difference in these binding energies.

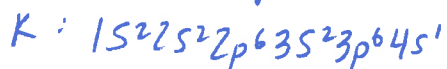
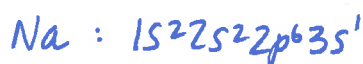
Na has 11 protons and K has 19; K has a larger nuclear charge. (The 1s electrons aren't shielded from the nucleus by other electrons). So potassium's 1s electrons will be more strongly attracted to the nucleus than sodium's 1s electrons, so potassium's electrons will need to absorb/increase energy more to leave the atom.

- g. For carbon and fluorine, compare the IE_1 values from the previous page – which element has a larger IE, and WHY? C: 1090 kJ/mole F: 1680 kJ/mole



Both atoms would lose a 2p electron, but F has 3 more protons than Carbon, so F has a higher effective nuclear charge. So F's electrons are more attracted to the nucleus than C's electrons, so need more energy to leave the atom.

- h. Why is the binding energy of sodium's 3s electron larger than the binding energy of the potassium's 4s electron? (In other words, why does sodium have a higher ionization energy than potassium?)



Both have an effective nuclear charge of +1, but Na's 3s electrons are closer to the nucleus than K's 4s electrons.

So Na's 3s e- are more strongly attracted to the nucleus, so they'll need more energy to leave the atom.

- i. Lithium, Cesium, and rubidium have IE_1 values of 376, 403, and 520 kJ/mole. Which element has which IE_1 value?

Cs Rb Li

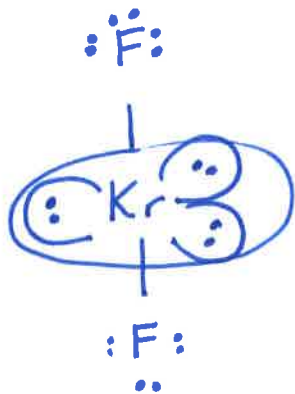
Li	520
Na	
K	
Rb	403
Cs	376

↑
IE increases

Problem K



(22)

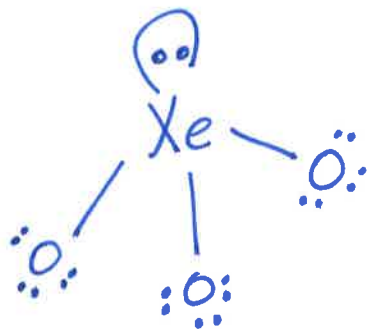


(e.g. = trigonal bipyramidal)
m.g. = linear

nonpolar due to symmetry.



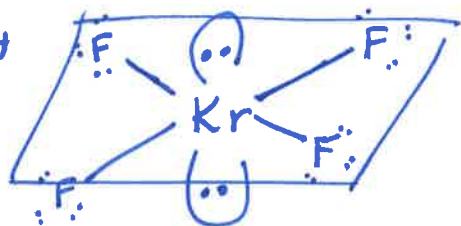
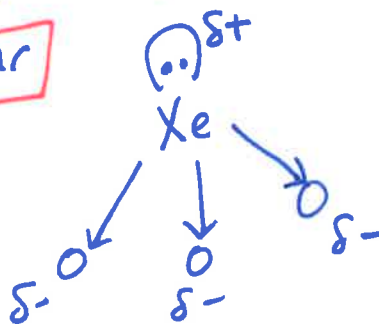
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(eg = tetrahedral)
mg = trigonal pyramidal

polar

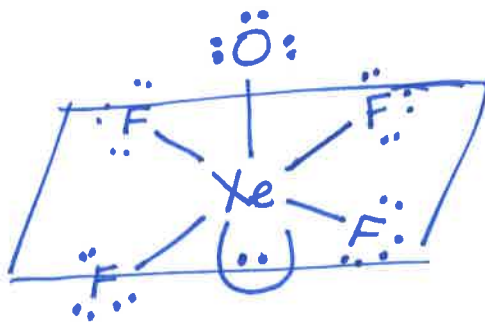
net polarity arrow



(e.g. = octahedral)
mg = square planar
nonpolar due to symmetry.



polar



↑ net polarity arrow up toward oxygen

(eg = octahedral)
mg = square pyramidal

the $Xe \rightarrow F$ polarities all cancel out, but the $Xe \rightarrow O$ polarity arrow doesn't cancel

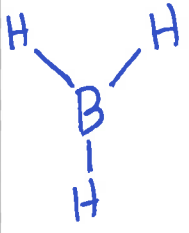
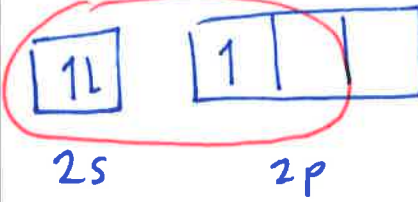
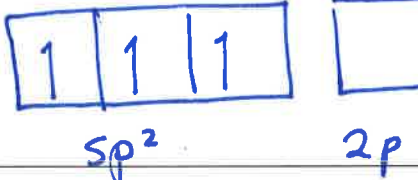
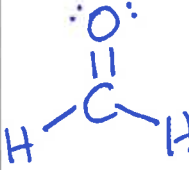
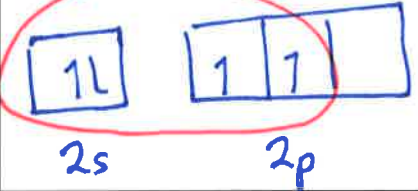
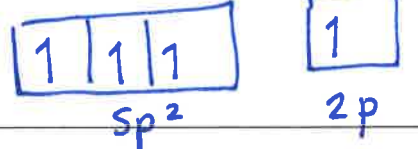

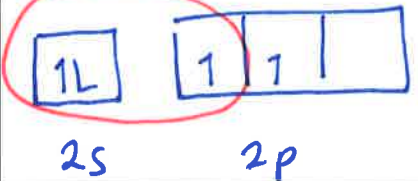
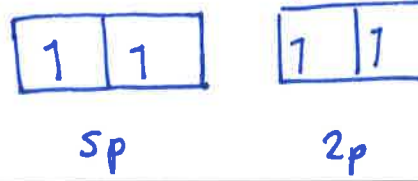
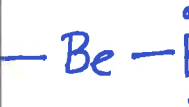
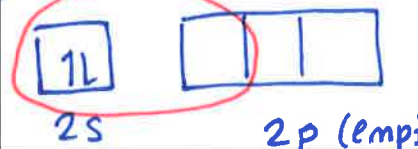

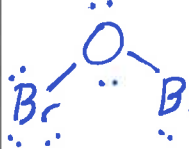
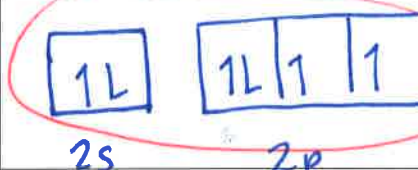

"Valence Bond Question" (the "VBQ")

Molecule	Draw Dot Structure	Draw the Orbital Filling Diagram of the Central atom (before hybridization) (everything since the last noble gas)	Draw the Orbital Filling Diagram of the Central atom (after hybridization) and state what the hybridization is.
CH ₄ ⑧		Carbon is $1s^2 2s^2 2p^2$ so, 	4 total pairs, so 109.5° , sp^3
C ₂ H ₄ ⑫		(pick one carbon as the "central atom") 	3 total "domains" so ideal bond \angle of 120° so, sp^2
C ₂ H ₂ ⑩		(pick one carbon as the "central atom") 	2 bonding domains 0 lone pairs 2 total domains so 180° and sp
NH ₃ ⑧		N is $1s^2 2s^2 2p^3$ 	4 domains (3+1) so 109.5° , sp^3 ideal \angle these are needed to make two π bonds.

these are the lone pair on N

these will be in the bonds with H

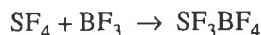
VBA Continued!

<p>BH₃</p> <p>(6)</p>		<p>Boron: 1s²2s²2p¹</p>  <p>2s 2p</p>	<p>3 total domains, so 120° and sp²</p>  <p>sp² 2p</p>	<p>empty since no π bonds are needed.</p>
<p>CH₂O</p> <p>(12)</p>		 <p>2s 2p</p>	<p>3 total domains, so ideal & ≠ 120° and sp²</p>  <p>sp² 2p</p>	<p>the carbon needs this half filled p orbital to form a π bond</p>
<p>HCN</p> <p>(10)</p>		 <p>2s 2p</p>	<p>2 total, 180°, sp</p>  <p>sp 2p</p>	<p>the carbon uses these to form π bonds two</p>
<p>BeF₂</p> <p>(Be doesn't get an octet)</p> <p>(16)</p>		<p>Beryllium 1s²2s²</p>  <p>2s 2p (empty)</p>	<p>2 domains, 180°, sp</p>  <p>sp 2p</p>	<p>empty. Be doesn't need to make any π bonds.</p>
<p>OBr₂</p> <p>(20)</p>		<p>Oxygen 1s²2s²2p⁴</p>  <p>2s 2p</p>	<p>2 bp + 2 lp = 4 total domains so 109.5° (ideal) and sp³</p>  <p>sp³</p>	<p>these will be the lone pairs on oxygen</p> <p>these will be in the bonds to Bromine.</p>

7. Answer the following questions about the structures of ions that contain only sulfur and fluorine.

2006

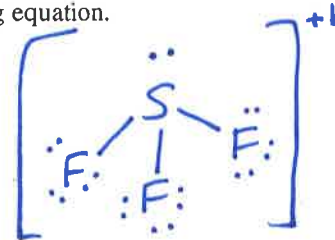
(a) The compounds SF_4 and BF_3 react to form an ionic compound according to the following equation.



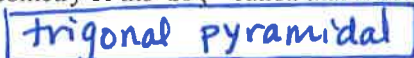
(i) Draw a complete Lewis structure for the SF_3^+ cation in SF_3BF_4 .

$$6 + 3(7) - 1 = 26 \text{ v.e.}$$

(ii) Identify the type of hybridization exhibited by sulfur in the SF_3^+ cation.



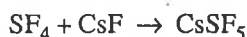
(iii) Identify the geometry of the SF_3^+ cation that is consistent with the Lewis structure drawn in part (a)(i).



(iv) Predict whether the F-S-F bond angle in the SF_3^+ cation is larger than, equal to, or smaller than 109.5° . Justify your answer.

The electron geometry of this ion is tetrahedral, which involves an "ideal" bond angle of 109.5° ; However, lone pairs of electrons repel bond pairs more strongly than the bond pairs repel each other, so the lone pair on the sulfur will push the S-F bonds away from it strongly, which will push the three S-F bonds closer to each other, probably to a couple of degrees less than 109.5° .

(b) The compounds SF_4 and CsF react to form an ionic compound according to the following equation.



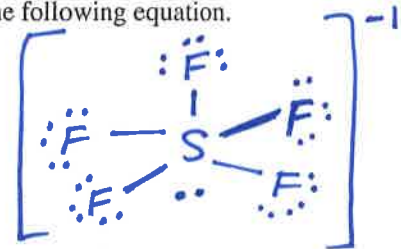
(i) Draw a complete Lewis structure for the SF_5^- anion in $CsSF_5$.

$$6 + 7(5) + 1 = 42$$

(ii) Identify the type of hybridization exhibited by sulfur in the SF_5^- anion.

(we used to say sp^3d^2 if 6 total e-pairs...)

(iii) Identify the geometry of the SF_5^- anion that is consistent with the Lewis structure drawn in part (b)(i).



2006

8. Suppose that a stable element with atomic number 119, symbol Q, has been discovered.

(The next noble gas after Rn would be #118, and in $7p^6$)

(a) Write the ground-state electron configuration for Q, showing only the valence-shell electrons.



(b) Would Q be a metal or a nonmetal? Explain in terms of electron configuration.

Q would be a metal. Its electron configuration ends in ns^1 , just like all of the alkali metals. It would be in the alkali metals column (IA), just below Francium.

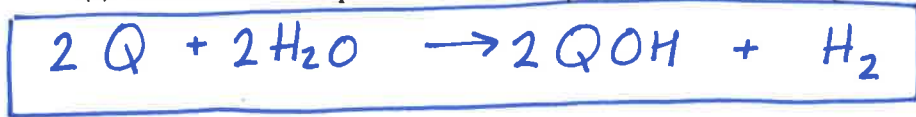
(c) On the basis of periodic trends, would Q have the largest atomic radius in its group or would it have the smallest? Explain in terms of electronic structure.

It would have the largest radius in its group. Radius increases as you go down a column, as the n-level of the outer (valence) electron increases. It would have similar effective nuclear charge to the elements above it, but its outer electron is in $n=8$. All the elements above it in its column have their outer

(d) What would be the most likely charge of the Q ion in stable ionic compounds?



(e) Write a balanced equation that would represent the reaction of Q with water.



electron in $n=7$ or lower. The higher the n-level, the larger the electron distance from the nucleus, so the larger the radius.

(f) Assume that Q reacts to form a carbonate compound.

(i) Write the formula for the compound formed between Q and the carbonate ion, CO_3^{2-} .



(ii) Predict whether or not the compound would be soluble in water. Explain your reasoning.

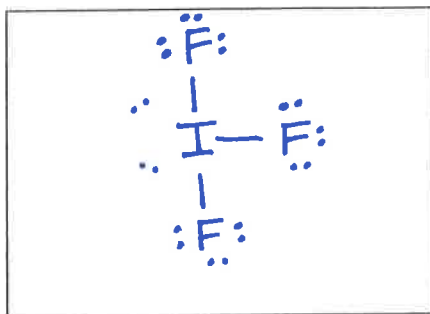
It would be expected to be soluble. It would contain Q^+ , an alkali metal cation. Ionic compounds containing alkali metal cations are generally soluble in water.

2007

6. Answer the following questions, which pertain to binary compounds.

$$7 + 7(3) = 28 \text{ v.e.}$$

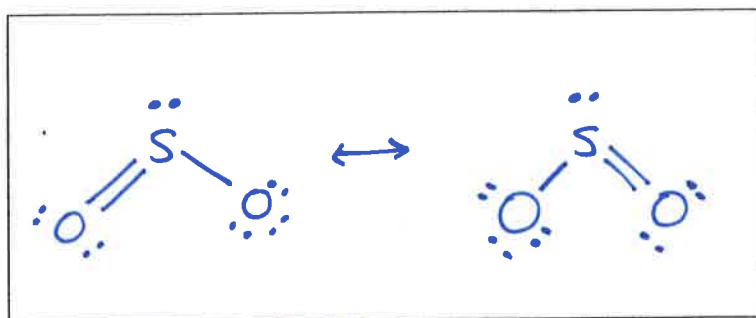
(a) In the box provided below, draw a complete Lewis electron-dot diagram for the IF_3 molecule.



(b) On the basis of the Lewis electron-dot diagram that you drew in part (a), predict the molecular geometry of the IF_3 molecule.

T-shaped

(c) In the SO_2 molecule, both of the bonds between sulfur and oxygen have the same length. Explain this observation, supporting your explanation by drawing in the box below a Lewis electron-dot diagram (or diagrams) for the SO_2 molecule. $6 + 2(6) = 18$



As shown above, SO_2 's double bond can be in either the left or right S-O bond; this molecule has resonance. The π bond is delocalized over both S-O bonds, so the two S-O bonds will be equal in length, and will be shorter than a typical S-O single bond, but longer than a typical S-O double bond.

(d) On the basis of your Lewis electron-dot diagram(s) in part (c), identify the hybridization of the sulfur atom in the SO_2 molecule.

Sp^2

2008

5. Using principles of atomic and molecular structure and the information in the table below, answer the following questions about atomic fluorine, oxygen, and xenon, as well as some of their compounds.

Atom	First Ionization Energy (kJ mol ⁻¹)
F	1,681.0
O	1,313.9
Xe	?

(a) Write the equation for the ionization of atomic fluorine that requires 1,681.0 kJ mol⁻¹.



(b) Account for the fact that the first ionization energy of atomic fluorine is greater than that of atomic oxygen. (You must discuss both atoms in your response.)

F: 1s²2s²2p⁵ O: 1s²2s²2p⁴
 Both elements would be losing an electron from n=2 (from a 2p orbital) when they form a +1 ion. Fluorine has 1 more proton than oxygen (9 compared to 8), so fluorine has a higher nuclear charge. The 2p electrons will be more attracted to the nucleus in fluorine than in oxygen, so fluorine's 2p electrons will require more energy to escape this attractive force and leave the atom.

(c) Predict whether the first ionization energy of atomic xenon is greater than, less than, or equal to the first ionization energy of atomic fluorine. Justify your prediction.

Xenon will have a smaller ionization energy than fluorine.
 F: 1s²2s²2p⁵ Xe: [Kr]5s²4d¹⁰5p⁶. Though Xenon's outer electron may experience a slightly higher effective nuclear charge than fluorine's outer electron, Xe would be losing a 5p electron, while F would be losing a 2p electron. n=5 electrons are further from the nucleus than n=2 electrons; Xe has a larger radius than F. According to Coulomb's law, the attractive force between the electrons and the nucleus will decrease as the distance between them increases. So Xenon's 5p electron will be less attracted to its nucleus than fluorine's e⁻ to its nucleus, so

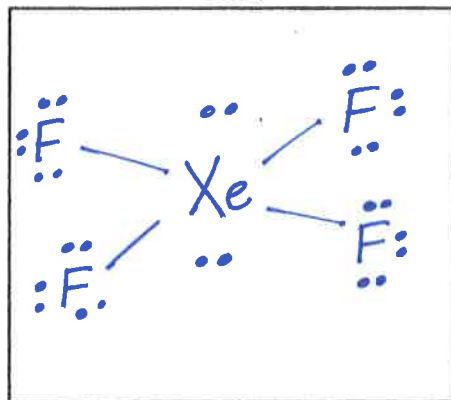
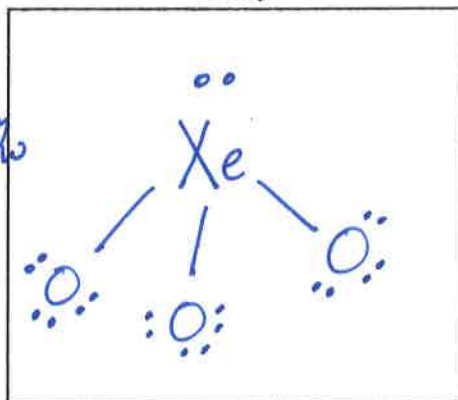
(d) Xenon can react with oxygen and fluorine to form compounds such as XeO₃ and XeF₄. In the boxes provided, draw the complete Lewis electron-dot diagram for each of the molecules represented below.

$$8 + 3(6) = 26$$

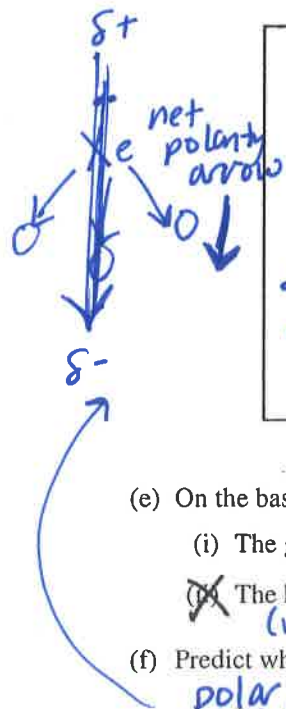
XeO₃

$$8 + 4(7) = 36$$

XeF₄



Xenon will require less energy to form a +1 ion/less energy to lose an electron.



(e) On the basis of the Lewis electron-dot diagrams you drew for part (d), predict the following:

(i) The geometric shape of the XeO₃ molecule trigonal pyramidal

(ii) The hybridization of the valence orbitals of xenon in XeF₄. (we would have said sp³d² since 6 total pairs) Shape = square planar

(f) Predict whether the XeO₃ molecule is polar or nonpolar. Justify your prediction.

polar, since the molecule is asymmetrical; the polarity arrows do not cancel. see picture above, to left of dot structure.

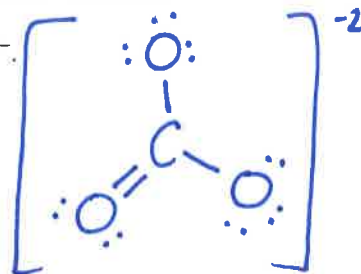
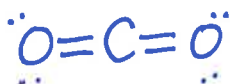
8. Answer the following questions using principles of chemical bonding and molecular structure.

1999

(a) Consider the carbon dioxide molecule, CO_2 , and the carbonate ion, CO_3^{2-} .

16 v.e

(i) Draw the complete Lewis electron-dot structure for each species.



(ii) Account for the fact that the carbon-oxygen bond length in CO_3^{2-} is greater than the carbon-oxygen bond length in CO_2 .

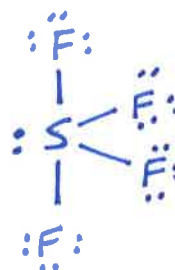
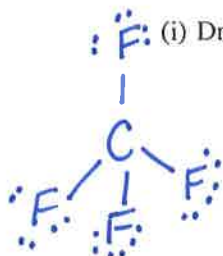
Single bonds are longer than double bonds. The C-O bonds in CO_2 are double bonds. In CO_3^{2-} , the π bond is delocalized over all three C-O bonds (it has resonance) so the three C-O bonds are the same length, and since they are more like "1/3" bonds, they are shorter than C-O single bonds, but longer than C-O double bonds (like those in CO_2).

(b) Consider the molecules CF_4 and SF_4 .

32 v.e.

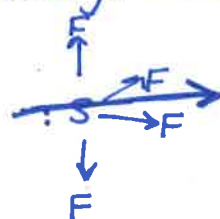
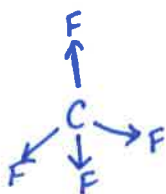
34 v.e.

(i) Draw the complete Lewis electron-dot structure for each molecule.



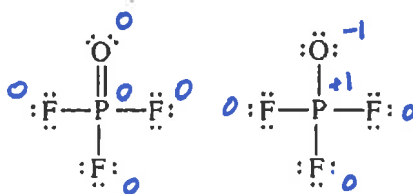
(ii) In terms of molecular geometry, account for the fact that the CF_4 molecule is nonpolar, whereas the SF_4 molecule is polar.

Both have polar bonds. However since CF_4 has no lone pairs and has tetrahedral molecular geometry, the molecule is very symmetrical, so the polarity arrows add to zero (it has no net dipole). \leftarrow the polarity arrows in CF_4 cancel out. SF_4 is asymmetrical due to the extra lone pair; it has a "seesaw" molecular geometry. It has a net polarity toward the two fluorines on the right side of the picture, as shown here:



2005

(c) Two Lewis structures can be drawn for the OPF_3 molecule, as shown below.



Structure 1

Structure 2

(i) How many sigma bonds and how many pi bonds are in structure 1? 4 sigma, 1 pi

(ii) Which one of the two structures best represents a molecule of OPF_3 ? Justify your answer in terms of formal charge. If we base our answer on formal charges, structure 1 is best. All of the formal charges are zero in structure 1. In structure 2, the fluorines have a zero formal charge, but the P is +1 and the oxygen is -1. It is best to have formal charges equal to zero, or as low as possible.

Periodic Trends

IE increases (usually)

- explain:
- why IE_1 of F > IE_1 (O)
 - " IE_1 (N) > IE_1 (O)
 - " IE_1 (Mg) > IE_1 (Ca)
 - " IE_1 (Mg) > IE_1 (Al)



(e) (a) and (c) obey the general periodic table trend (F is to the right of O, Mg is above Ca) ... (b) and (d) do not.

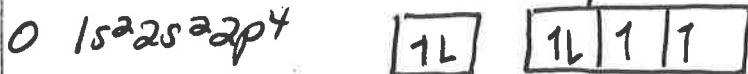
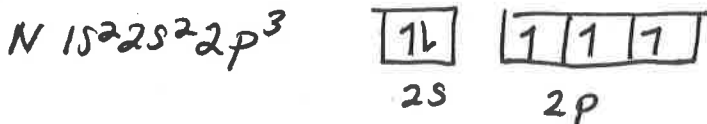
- (a)
- | | | |
|---|------------------|----------------------|
| F | $1s^2 2s^2 2p^5$ | 9 protons in nucleus |
| O | $1s^2 2s^2 2p^4$ | 8 protons in nucleus |

Fluorine has a higher effective nuclear charge than oxygen. The outer electrons in F and O are shielded from the nucleus by the negative electrons in ~~the~~ the 1s level, so

Fluorine has an effective nuclear charge of $9 - 2 = +7$
 oxygen " " " " $8 - 2 = +6$

This will cause Fluorine's radius to be smaller than oxygen's. The outer electron will be closer to the nucleus, and will be more strongly attracted to the higher charged nucleus, so will be harder to remove. (Coulomb's Law $F = \frac{kq_1 q_2}{r^2}$ so larger charge nucleus and shorter distance will each cause higher attractive force.)

(b) N vs O



oxygen does have a higher effective nuclear charge and smaller radius than nitrogen. these factors would make oxygen's ionization energy higher.

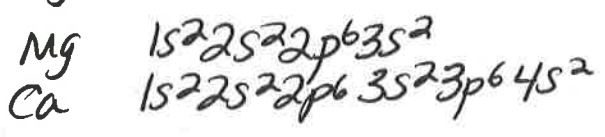
However, Nitrogen's 2p energy level is exactly half-filled, which corresponds to a relatively low potential energy because the electrons each have their own orbital to exist in.

Since the electrons in nitrogen start at a lower potential energy than the ones in oxygen, nitrogen's electrons will require more energy to leave the atom.

Trends

periodic table Question (cont'd)

c) Mg vs Ca why does Mg have higher IE



Mg and Ca's outer electrons experience similar "effective nuclear charge".

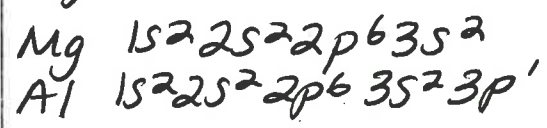
Mg: 12 protons, 10 "inner electrons" → +2 effective nuclear charge
Ca: 20 protons, 18 "inner electrons" → +2 effective nuclear charge

However, Calcium has a larger radius than Mg since its outer electrons are in $n=4$ instead of $n=3$.

Therefore ~~the~~ ^{Ca's} electrons won't experience as much attractive force to the nucleus and will be easier (will require less energy) to remove, acc. to Coulomb's Law.

(or: the electrons in Ca start at a higher energy level.. $n=4$ vs $n=3$, so don't need to gain as much potential energy in order to leave).

d) Mg vs Al why does Mg have higher IE?



Al has higher effective nuclear charge and smaller radius than Mg, which would lead to a higher IE for Al vs Mg.

However, Al's outer electron is in the 3p energy level, and Mg's is in 3s. Since the Al's electron starts in a higher energy level, it doesn't need to gain as much potential energy to be able to leave the atom.

Also, Mg having a filled or half-filled energy level leads to low potential energy.. Mg starts with a filled s-level (low potential energy) so will need a lot of potential energy to lose this e-.