Chem 130 – Second Exam Key

Name______________________________

On the following pages you will find questions that cover the structure of molecules, ions, and solids, and the different models we use to explain the nature of chemical bonding. Read each question carefully and consider how you will approach it before you put pen or pencil to paper. If you are unsure how to answer one question, then move on to another question; working on a new question may suggest an approach to the one that is more troublesome. If a question requires a written response, be sure that you answer in complete sentences and that you directly and clearly address the question.

Question 1 _____/18	Question 5 _____/14
Question 2 _____/12	Question 6 _____/10
Question 3 _____/12	Question 7 _____/10
Question 4 _____/12	Question 8 _____/12

Total _____/100

Some potentially useful equations and constants are provided here. A periodic table and other potentially useful data are provided on a separate handout.

$c = \lambda\nu$ $E = h\nu$ $KE = h\nu - W$

$$\frac{1}{\lambda} = 1.09737\times10^{-2}\ \text{nm}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$V \propto \frac{Q_+ Q_-}{d}$$

$$\text{AVEE} = \frac{xIE_s + yIE_p + zIE_d}{x + y + z}$$

(valence shell electrons only)

$$\text{FC}_a = V_a - N_a - \frac{B_a}{2}$$

$$\delta_a = V_a - N_a - B_a\left(\frac{EN_a}{EN_a + EN_b}\right)$$

$c = 2.998\times10^8$ m/s $h = 6.626\times10^{-34}$ Js $N_A = 6.022\times10^{23}$ mol^{-1}

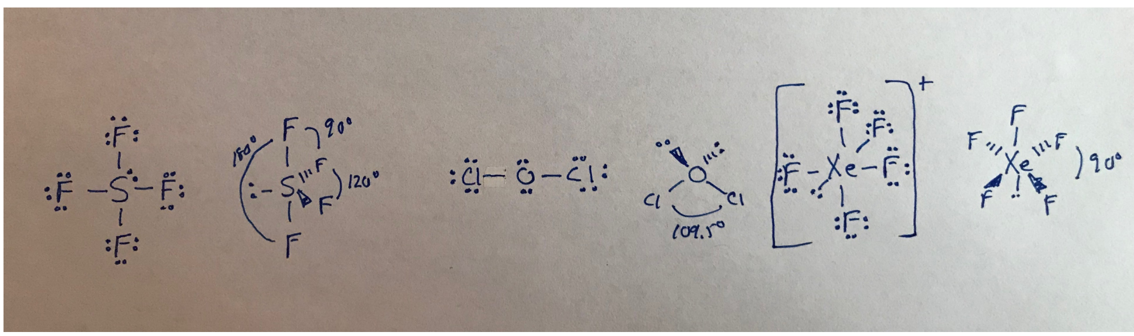
Problem 1. For each of the following molecules or ions, draw **one** valid Lewis structure, which need not be the "best" structure. Give the name for the bonding geometry around the underlined central atom, predict whether the molecule or ion is polar or is non-polar, and give the idealized bond angles for the stated bonds; if there is more than one possible bond angle, then list each unique bond angle and annotate your Lewis structure to indicate which is which. *Your answers for these last two items must be consistent with the bonding geometry you identify*.

The figures below show the Lewis structures; the VSEPR diagrams are included as an aid for visualizing the bonding geometry, for determining polarity, and for labeling the bond angles.

SF_4: There are 6 + (4 × 7) = 34 valence electrons, which gives the Lewis structure shown below. With four bonding domains and five electron domains, the bonding geometry is see-saw with ideal bond angles of 90° (axial to equatorial), 120° (equatorial to equatorial), and 180° (axial to axial). The molecule is polar.

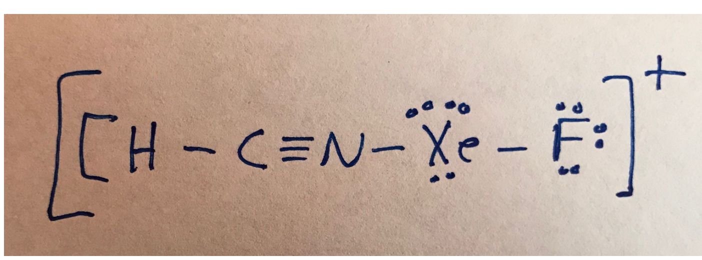
OCl_2: There are 6 + (2 × 7) = 20 valence electrons, which gives the Lewis structure shown below. With two bonding domains and four electron domains, the bonding geometry is bent with ideal bond angles of 109.5°. The molecule is polar.

XeF_5^+: There are 8 + (5 × 7) – 1 = 42 valence electrons, which gives the Lewis structure shown below. With five bonding domains and six electron domains, the bonding geometry is square pyramidal with ideal bond angles of 90°. The ion is polar.

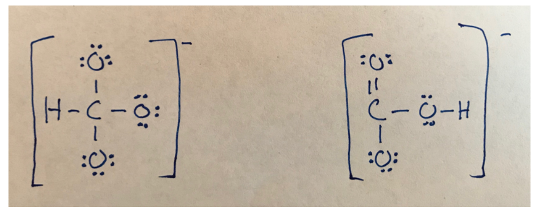


Problem 2. The cation $[HCNXeF]^+$ is interesting both because it is an example of a species that includes an element, Xe, normally thought of as inert, and because it is perfectly linear; that is, the HCN, CNXe, and NXeF bonds all have bond angles of 180°. Draw a Lewis structure for this cation that explains this linear structure and identify the element that carries the positive charge.

There are 1 + 4 + 5 + 8 + 7 – 1 = 24 valence electrons to account for. The linearity requires two bonding domains for each of C, N, and Xe, which allows for only one possible Lewis structure, as shown here. Note that there are five electron domains around Xe, three of which (in equatorial positions) hold lone pairs of electrons.



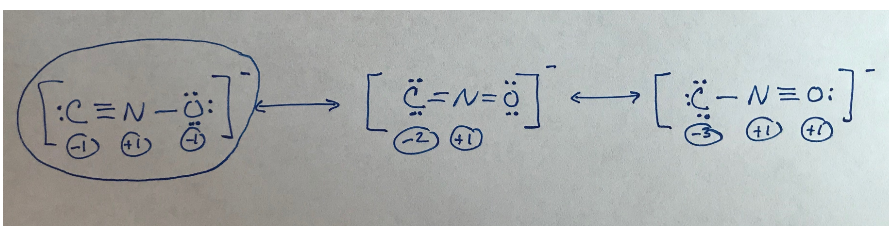
Problem 3. The bicarbonate ion is HCO_3^-, where each oxygen is attached to the carbon. As written, the formula also seems to suggest that the hydrogen is attached to the carbon when actually it is attached to one of the three oxygens. Using one or more of the bonding models developed in this unit, present a convincing argument that the hydrogen is attached to the oxygen and not to the carbon. Your written response should require no more than a single paragraph of 3–5 sentences, accompanied with suitable sketches.



We cannot apply the molecular orbital model because a MO diagram is not provided to us. The bicarbonate ion has $1 + 4 + (3 \times 6) + 1 = 24$ valence electrons to account for in a Lewis structure, which is the starting point for all other bonding models. The Lewis structure on the left shows that attaching the hydrogen to carbon requires 26 electrons if it is to obey the octet rule. To reduce this to 24 electrons requires moving a lone-pair of electrons to make a double bond between an oxygen and carbon, which then violates the octet rule for carbon. The Lewis structure on the right shows that attaching the hydrogen to one oxygen and forming a single bond and a double bond between carbon and the other two oxygens requires 24 electrons.

Problem 4. Fulminate, CNO^-, is a particularly unstable anion whose mercury salt is used as the explosive compound in blasting caps. Draw all possible resonance structures for the fulminate anion and report the formal charge on each atom in each structure. The bonding framework for fulminate is C–N–O.

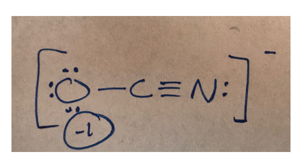
Fulminate has $4 + 5 + 6 + 1 = 16$ valence electrons, which allows for these resonance structures (and formal charges for use in next question).



Which of your resonance structures provides the best picture of the bonding in fulminate? Circle your choice above and then explain your reasoning below in 1–2 sentences.

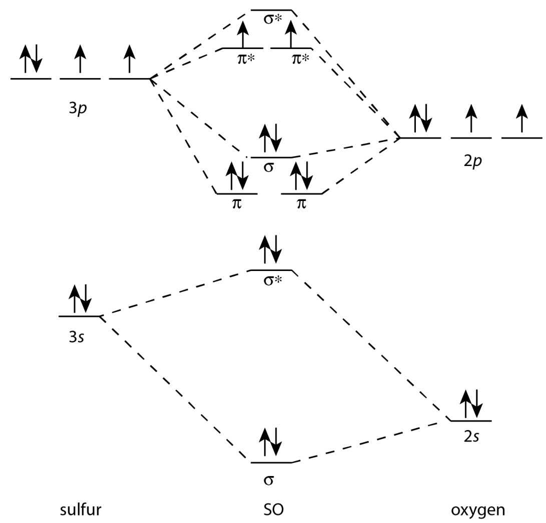
The most important of the three resonance structures is the one circled above as all formal charges are +1 or –1, and, although it does include a formal charge of –1 on the least electronegative atom (carbon), it also includes a formal charge of –1 on the most electronegative atom (oxygen).

The most important resonance structure for cyanate, OCN^-, has a single bond between the oxygen and the carbon, and a triple bond between the carbon and the nitrogen. Using your resonance structures for fulminate and the information here about cyanate, provide a 1–2 sentence explanation for why fulminate is so explosive while cyanate is very stable.



The most important Lewis structure for cyanate, as shown here, has a formal charge of –1 on the more electronegative oxygen and formal charges of 0 on carbon and on nitrogen. All three resonance structures for fulminate, however, have a negative formal charge on the carbon, which makes fulminate much more reactive.

Problem 5. Sulfur monoxide, SO, is a simple inorganic molecule that is stable at very small concentrations only. It is rarely found on earth, but is found in a variety of interstellar environments, including the atmospheres of Io, one of Jupiter's moons, Venus, and the Hale-Bopp comet. The valence-shell molecular orbital diagram for SO is shown on the right. Complete the molecular orbital diagram by (a) identifying which atom is on the left side and which is on the right side, (b) labeling the valence-shell atomic orbitals with their appropriate *ns* and *np* designations, (c) adding the appropriate number of electrons to the atomic orbitals, and (d) adding the appropriate number of electrons to the molecular orbitals.



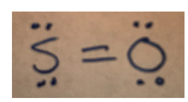
The complete molecular orbital diagram shows that (a) sulfur is on the left and oxygen is on the right, that (b and c) sulfur's valence shell is $3s^2 3p^4$ and oxygen's valence shell is $2s^2 2p^4$, and that (d) the 12 total valence electrons fill the molecular orbitals from the bottom-to-top, filling each molecular orbital before moving on to the next, and placing single electrons in each degenerate molecular orbital before pairing up electrons.

With respect to (a), in 1–2 sentences, explain how you determined which set of atomic orbitals belongs to sulfur.

Sulfur's valence shell is $n = 3$ and oxygen's valence shell is $n = 2$. As it is easier to remove an $n = 3$ electron than an $n = 2$ electron, sulfur's atomic orbitals must be less negative and higher up on the energy axis; thus, sulfur is on the left and oxygen is on the right.

With respect to (d), based on your molecular orbital diagram, what is the bond order between sulfur and oxygen? Does this agree with the bond order predicted by a Lewis structure? Be sure to support your answers with suitable structures, calculations, and/or a 1–3 sentence explanation.

The MO diagram has 8 electrons in bonding molecular orbitals and four electrons in antibonding molecular orbitals, which gives the bond order as $(8 - 4)/2 = 2$. This agrees with the Lewis structure, which is shown to the right.



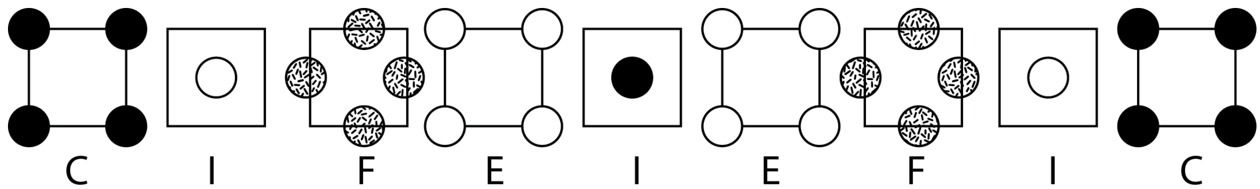
With respect to (d), what, if anything, can you conclude about the ability of SO to interact with an applied magnetic field. Explain your reasoning in 1–2 sentences.

The molecular orbital diagram shows two unpaired electrons in π* antibonding orbitals. Unpaired electrons makes SO paramagnetic, which means that it will interact with an applied magnetic field.

Problem 6. Consider the following three ionic compounds: MgF_2, SrF_2, and BeF_2. Which of these compounds has the largest melting point? Briefly justify your choice in 2–4 sentences.

The stronger the ionic bond, the higher the melting point. To estimate the strength of an ionic bond, we use Coulomb's law, which states that the strength of the bond is proportional to (Q_+Q_-/d), where Q_+ and Q_- are the charges of the ion and d is distance between them. The cations all have charges of +2 and the fluoride ions all have charges of –1; thus, it is the smallest d that matters here. The smallest of the cations is beryllium as its valence shell is $n = 2$, which makes BeF_2 the compound with the largest melting point.

Problem 7. The figure below shows nine cross-sections through the unit cell of a compound that consists of cerium (Ce: solid black spheres), gold (Au: speckled spheres), and silicon (Si: solid white spheres), where the left side is the bottom of the unit cell and the right side is the top of the unit cell (the values for *z* are, left-to-right, 0, 0.125, 0.250, 0.375, 0.500, 0.625, 0.750, 0.875, and 1.00). The compound is of interest because of its magnetic and superconducting properties. Using this unit cell, what is the simplest formula for this compound. Be sure that it is clear how you arrived at your formula.



The figure above shows the position of each atom in the unit cell using C to identify a corner shared by eight unit cells, E to identify an edge shared by four unit cells, F to identify a face shared by two unit cells, and I to identify a location wholly within the unit cell. The composition of the unit cell is

- for Ce (the solid black spheres), there are (8 × 1/8) + (1 × 1) = 2 atoms
- for Au (the speckled spheres), there are (8 × 1/2) = 4 atoms
- for Si (the solid white spheres), there are (8 × 1/4) + (2 × 1) = 4 atoms

The simplest formula, therefore, is $CeAu_2Si_2$.

Problem 8. Shown below is a list of hypothetical elements along with their electronegativities and possible charges (note that each element also has a possible charge of zero).

element	Ax	Ay	Cy	Cg	Ny	Kt	Wt	Lt	Bt	Z	Tx
electronegativity	0.92	0.94	1.51	2.89	2.03	0.82	3.82	1.03	1.63	2.31	2.55
charges (0, …)	+1	+2	+2, +3	+2	–2	+1	–1	+2	+1, +3	+1	+1

Using the information in this table, give the formula of (a) the most ionic-like compound, (b) the most metallic-like compound, and (c) the most covalent-like compound. Each of your three compounds must contain **two different elements**. In no more than three sentences, explain the reasoning behind your choices.

The most ionic-like compound is the one with largest value for ionicity, ΔEN, which in this case is between Kt and Wt, with, given their charges of +1 and of –1, a formula of KtWt and a ΔEN of 3.00. The most covalent-like compound is the one with largest value for covalency, $\overline{EN}$, which in this case is between Wt and Cg with, given their charges of +2 and of –1, a formula of $CgWt_2$ and an $\overline{EN}$ of 3.36. The most metallic-like compound is the one with the smallest value for covalency, which in this case is Kt and Ax with, because both are present in elemental form, a formula of AyKt and an $\overline{EN}$ of 0.87. Other reasonable choices for more metallic-like bonding are CgZ, CgTx, and ZTx, and AxAy for more covalent-like bonding.