Dr. Zellmer
Time: 7 PM Sun.
40 min

Chemistry 1250
Spring Semester 2022
Quiz VI

T, R
February 27, 2022

Name KEY Rec. TA/time

1. (5 pts) Show the relationship between lattice energy (LE), charge and distance between the charges and use it to explain which compound in each pair should have the greater LE.

a) show the equation for lattice energy, LE.

$$LE \propto \frac{Q_1 Q_2}{d}$$

Q = charges on ions d = distance between cation and anion (sum of ionic radii)

This eqn. shows the **LE** is **proportional** to the **charges** on the ions. The bigger the charges the greater the LE. (Use the magnitude, absolute value, of the charges).

The eqn also shows the **LE** is **<u>inversely</u> proportional** to the **distance between** the **charges**. The smaller the distance (the smaller the ions) the greater the LE.

b) $FeBr_3$ or $FeBr_2$

$FeBr_2$ +2 on Fe^{2+} and −1 on Br^-
$FeBr_3$ +3 on Fe^{3+} and −1 on Br^-

Fe^{3+} is smaller than Fe^{2+} so the FeBr distance is smaller in $FeBr_3$ than in $FeBr_2$.

The numerator for $FeBr_3$ is greater than that for $FeBr_2$ (3 to 2) and the distance between the ions in $FeBr_3$ is smaller than that in $FeBr_2$. Thus the expected result would be,

$$LE_{FeBr3} > LE_{FeBr2}$$

c) CaO or MgO

CaO +2 on Ca^{2+} and −2 on O^{2-}
MgO +2 on Mg^{2+} and −2 on O^{2-}

Mg^{2+} is smaller than Ca^{2+} so the MgO distance is smaller than the CaO distance

The numerators for CaO and MgO are the same (4). Since the distance between the Mg^{2+} and O^{2-} ions is smaller than that between Ca^{2+} and O^{2-} the denominator for LE is smaller and thus,

$$LE_{MgO} > LE_{CaO}$$

2. (3 pts) The dipole moment of ClF(g) is 0.88 D. The bond length is 1.63 Å. (**Show work and explain!**) What magnitude of the effective charge (i.e. the partial charge), in units of *e*, on the Cl and F atoms leads to this dipole moment?

A dipole occurs when you have two opposite charge separated by some distance. The quantative measurement of the magnitude of the dipole is the dipole moment, μ, when there are two equal and opposite charges is given by,

$$\mu = Q \bullet r \qquad Q = \text{charge} \quad r = \text{distance between charges}$$

For this problem you are after Q, the charge on the atoms which gives the experimental dipole moment.

$$Q = \frac{\mu}{r} = \frac{0.88\ \text{D}}{1.63\text{Å}} = 0.5\underline{\mathbf{3}}98\ \text{D/Å}$$

Need to covert this to units of *e* (electron charge):

$$\text{charge in } e = \frac{0.5\underline{\mathbf{3}}98\ \text{D}}{\text{Å}} \times \frac{3.34 \times 10^{-30}\ \text{C}\bullet\text{m}}{\text{D}} \times \frac{1\ \text{Å}}{10^{-10}\ \text{m}} \times \frac{1\ e}{1.602 \times 10^{-19}\ \text{C}}$$

$$= 0.1\underline{\mathbf{1}}25\ e = 0.11\ e$$

The more electronegative atom will have the partial negative charge, with a few exceptions (like in CO). Since **F** is **more electronegative** than Cl it will pull the electrons in the bond toward it and the partial negative chg will be on F and the partial positive chg on Cl.

$$\overset{\delta+}{\text{Cl}} - \overset{\delta-}{\text{F}}$$

3. (5 pts) Draw the Lewis structure of the selenite ion, SeO_3^{2-}, conforming to the Lewis octet (noble gas) rule, **and** put the formal charges on each atom. **(Must show work or explain what you are doing and show and account for all valence electrons and formal charges.)**

a) Lewis structure of SeO_3^{2-} ; Se: Grp 6A (6 val e^-) O: Grp 6A (6 val e^-)

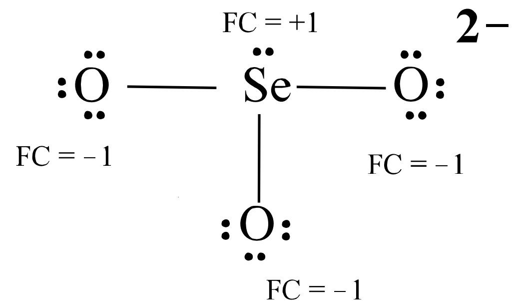
1) A = 1(6e⁻) + 3(6e⁻) + 2 e⁻ = 26 e⁻ available (Se, O, -2 chg)

$A = \underset{Se}{1(6e^-)} + \underset{O}{3(6e^-)} + \underset{-2\ chg}{2\ e^-} = 26\ e^-$ available

2) Draw skeleton structure. The more EN O atoms attached to Se This accounts for 6 e^-.

3) Put 6 e^- on each O to fulfill octet. This uses 18 e^-.

4) # e^- left = 26 e^- - (6 e^- + 18 e^-) = 2 e^-
These go on the Se atom to fulfill octet.



NOT trigonal planar, tetrahedral or flat T- shaped

5) Formal Charge:

Divide e^- in bonds equally between atoms (each atom gets ½ the e^- involved in the bond).

lpe⁻ assigned to the atom they're on.

Subtract this total from the valence e^- on the atom.

Ex: For Se: 6 - (3 + 2) = +1
For O: 6 - (1 + 6) = −1

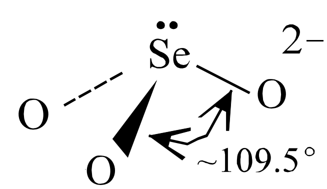
FC should add up to give overall chg., in this case −2 (as they do)

***** The following was not asked for *****

b) What is the shape of this species (polyatomic ion)?

4 e^- pairs (3 atoms & 1 lpe⁻) on Se
All 4 e^- pairs are arranged in a tetrahedron so angles start out close to 109.5°

- describe molecular shape by considering **only atoms** an **NOT lone pair e⁻**



trigonal pyramidal

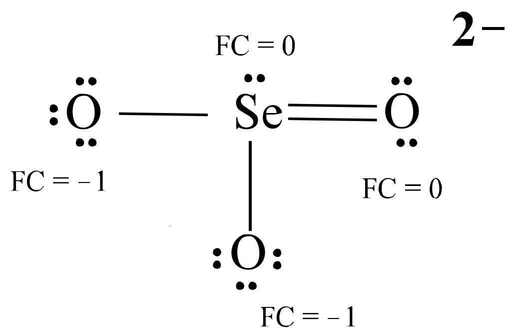
c) What is the O-Se-O bond angle?

< 109.5° or ~ 109.5° (but **NOT exactly** 109.5°)

The e^- pair (lpe⁻) on Se causes the angles to be slightly diff. than the 109.5° found in a perfect tetrahedral molecule (4 identical surrounding atoms).
For 4 "things" (atoms & lpe⁻) around a central atom, if all 4 things are **NOT identical** then angles are < 109.5° or ~ 109.5° (but NOT exactly 109.5°).

4. (5 pts) Draw the Lewis structure of the selenite ion, SeO_3^{2-}, conforming to the Formal Charge rules, **and** put the formal charges on each atom. **(Must show work or explain what you are doing and show and account for all valence electrons and formal charges.)**

Use the work done above in #6 to come up with this structure by remembering that from row 3 down atoms can get more than an octet around them, like I showed for SO_4^{2-} in lecture.



Still trigonal pyramidal

Atoms in row 3 and below can have more than an octet. Thus, the Se atom can form another bond to lower the formal charges. The above structure is one of three resonance structures with a double bond between the Se and one of the O atoms. The double bond appears to "move" between O atoms and the Se atom. However, remember for resonance structures none of them actually exists. Instead the actual structure is an average of all the resonance structures.

Based on formal charge rules, this structure would be better than the one in question 6. In the structure in this question, the formal charges are lower in all than those in question 6. In this structure only two atoms have formal charges that are nonzero, whereas the one in question 3 all atoms have nonzero formal charges. Also, the sum of the absolute values of the formal charges in the above structure is 2, which is lower than that in question 6, which is 4.

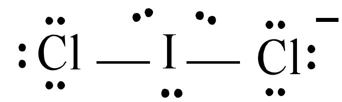
Actually, there are 4 resonance structures altogether, the 3 which look like the one above with the double bond in the different Se-O positions and the one above in question 6 which conforms to the octet rule.

Remember, there is disagreement on whether the octet rule or formal charge rules should take precedence. We would ask you to draw the structure conforming to one or the other rule, like I did in question 6 and this question.

5. (5 pts) Draw the Lewis structure for ICl_2^-. How many lone pair(s) of electrons are there in the valence shell of the central atom?

I: 7A Cl: 7A −1 chg
I Cl 1 e^-
1) A = 1(7e-) + 2(7e-) + (1e-) = 22 val e^-

2) Draw skeleton structure. The more EN Cl atoms attached to I This accounts for 4 e^-.



Iodine is in the middle

3) Put 6 e^- on each Cl to fulfill octet. This uses 12 e^-.

4) # e^- left = 22 e^- - (4 e^- + 12 e^-) = 6 e^-
These go on the I atom. This gives 10 e- on the I atom, more than an octet.

I has 2 bonds & 3 lpe^- in this case since it is in the middle (when halogens are on the outside they have only 1 bond)

The ED geometry around the I is trigonal bipyramidal and the molecular geometry is linear with a bond angle of 180°

6. (8 pts) Draw the all the possible resonance structures of the cyanate ion, NCO^-, conforming to the Lewis octet rule **<u>and</u>** put the **formal charges** on each atom. **Also**, **indicate** which would likely be the **dominate structure**. **(Must show work or explain what you are doing and show and account for all valence electrons and formal charges. Also, explain your reasoning for your choice of the dominate structure.)**

a) Lewis structure of NCO^- ; N: Grp 5A (5 val e^-) C: Grp 4A (4 val e^-) O: Grp 6A (6 val e^-)

$$\begin{matrix} & N & & C & & O & -1\text{ chg} \\ 1)\ A = & 1(5e^-) & + & 1(4e^-) & + & 1(6e^-) & + 1\ e^- = 16\ e^-\text{ available} \end{matrix}$$

2) Draw skeleton structure. The more EN N & O atoms attached to C.
This accounts for 4 e^-. This will leave 12 e^-.

N - C - O

3) Put 6 e^- on N & O to fulfill octet. This uses 12 e^-.

: N̤̈ - C - Ö̤:

4) # e^- left = 16 e^- - (4 e^- + 12 e^-) = 0 e^-

The C doesn't have an octet (C normally forms 4 bonds).
Need to "take" e^- from N or O to form multiple bonds.
Get resonance structures.

5) Formal Charge:

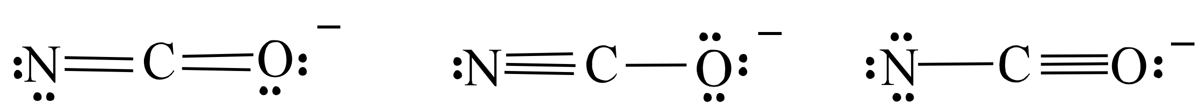
Divide e^- in bonds equally between atoms
(each atom gets ½ the e^- involved in the bond).

lpe^- assigned to the atom they're on.

Subtract this total from the valence e^- on the atom.

Ex: For N: 5 - (2 + 4) = −1
For C: 4 - (4 + 0) = 0
For O: 6 - (2 + 4) = 0

FC should add up to give overall chg., in this case −1 (as they do)



FC = −1 FC = 0 FC = 0   FC = 0 FC = 0 FC = -1   FC = −2 FC = 0 FC = +1

The **second structure** would be the **dominate one** in this case since the neg. FC is on the more EN O atom. The third structure would not contribute much since the sum of the absolute values of the FC is the largest and the N atom has a -2 and the O has a +1, which would not normally be the case since O is more EN.

7. (3 pts) Of the possible bonds between nitrogen atoms (single, double, and triple), this of the following are ture? Multiple answers possible.

a) a triple bond is longer than a single bond
b) a double bond is stronger than a triple bond
c) a single bond is stronger than a triple bond
d) a double bond is longer than a triple bond
e) a single bond is stronger than a double bond
f) a triple bond is stronger than a double bond

Both D and F are true. When the same two atoms are involved the following is true for the bond lengths (in order of decreasing length) and strengths (in order of increasing strength) :

single < double < triple

double bonds are shorter than single bonds and triple bonds are shorter than double bonds

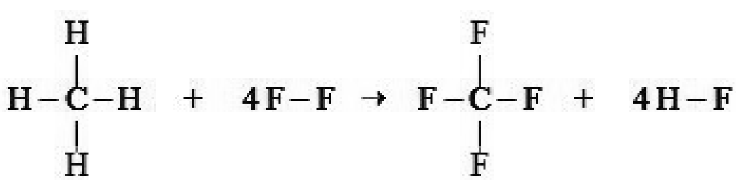
double bonds are stronger than single bonds and triple bonds are stronger than double bonds

Think of bonds like springs. A double bond is a shorter fatter spring than a single bond and thus it takes more energy to break a double bond. A triple bond is a shorter fatter spring than a double bond and thus it takes more energy to break a triple bond.

8. (4 pts) Use the given bond enthalpy data to estimate the ΔH° (kJ) for the following gas phase reaction

C - H = 413 kJ, H - F = 567 kJ, F - F = 155 kJ, C - F = 485 kJ

$$CH_4\,(g) \; + \; 4\,F_2\,(g) \; \rightarrow \; CF_4\,(g) \; + \; 4\,HF\,(g)$$



Use bond enthalpies to determine the ΔH_{rxn}. You will see bond enthalpies as BE(bond) or D(bond).

$$\Delta H_{rxn} \;=\; \sum BE_{broken} \;-\; \sum BE_{formed}$$

$$\Delta H^\circ \;=\; [(4)\,D(C-H) \;+\; (4)\,D(F-F)] \;-\; [(4)\,D(C-F) \;+\; (4)\,D(H-F)]$$

$$\Delta H^\circ \;=\; [(4)\,(413\text{ kJ}) \;+\; (4)\,(155\text{ kJ})] \;-\; [(4)\,(485\text{ kJ}) \;+\; (4)\,(567\text{ kJ})]$$

$$= [2272\text{ kJ}] \;-\; [4208\text{ kJ}]$$

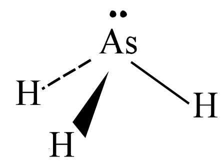
$$= -1936\text{ kJ}$$

9. (6 pts) Consider the following molecules and list their **__molecular__ shapes** (NOT the electron domain geometries), **__bond angles__** and whether they are **__polar or nonpolar__**. (**Provide the Lewis structure and a short explanation for your choices.**)

1) AsH_3

trigonal pyramidal (≈ 109.5° angles)
4 things around As and not all identical
(3 H and **1 lpe$^-$**)

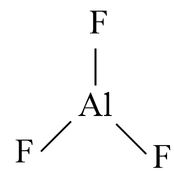
Polar (like **:**NH_3,**:**PH_3, **:**PCl_3, etc.)



2) AlF_3

trigonal planar (120° angles, exactly)
3 things around Al and **__all__ identical**
(3 atoms and **NO lpe$^-$**)

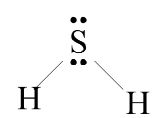
__Non__polar (like BCl_3, BF_3 $AlCl_3$ etc.)



3) H_2S

bent: 4 things around S and not all identical (2 H and **2 lpe$^-$**)
lpe$^-$ on O (≈ 109.5° angles)

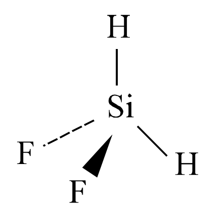
Polar (like $H_2\ddot{O}$**:**, $H_2\ddot{S}$**:**, etc.)



4) SiH_2F_2

tetrahedral (≈109.5° angles)
all 4 atoms on Si are **__not__** identical

Polar (like $CHCl_3$, CH_3Cl, CH_2Cl_2, ect.)



NOTE: The **5 basic symmetric** molecular **geometries** (linear, trigonal planar, tetrahedral, trigonal bipyramidal and octahedral) can give **non**polar if all *surrounding* **atoms** (or groups of atoms) are **__identical__** to each other (although they don't all have to be identical for the trigonal bipyramidal, octahedral or square planar molecular geometries.

See Tables 9.2 and 9.3 on pages 350 and 353 in the textbook.

***** continued on the next page *****

9. (Cont.)

* **NOTE**: If there are 1 or more **lpe$^-$** on the central atom the molecule will **generally** be **polar**.

There are two shapes that can be exceptions to this ‘rule’. (See Table 9.3 on page 353 of the textbook.)

The linear shape resulting from the trigonal bipyramidal e$^-$-pair geometry will be nonpolar if the 2 atoms around the central atom are identical to each other (e.g. XeF_2 has 3 lpe$^-$ in a trigonal planar geometry around the Xe and the 2 F atoms linear to each other).

The square planar shape resulting from the octahedral e$^-$-pair geometry will be nonpolar if the 4 atoms around the central atom are identical to each other (e.g. XeF_4 has 4 F atoms in a square planar arrangement with 2 lpe$^-$ linear to each other, 1 above and 1 below the square planar arrangement).

For AlF_3 (#2) it’s trigonal planar & **all atoms** *surrounding* Al are **identical** so the molecule is **non**polar.

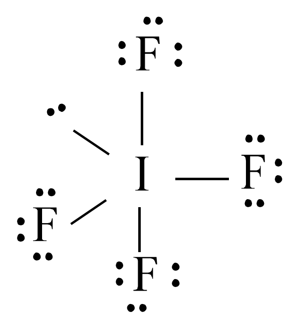
H_2S and AsH_3 (3 & 1) neutral molecules which are bent or trigonal pyramidal with **lpe$^-$** on the central atom are **polar**. In general, molecules that have **<u>1</u>** or **<u>more</u> <u>lpe</u>$^-$** on the **<u>central</u> <u>atom</u>** are **<u>polar</u>**. (See discussion above about exceptions.)

For SiH_2F_2 (#4) it is tetrahedral but all surrounding atoms are **<u>NOT</u> identical** so the molecule is **<u>polar</u>**.

10. (6 pts) Draw the Lewis structure of IF_4^+. What is its electron-domain geometry? What is its molecular geometry? What are the bond angles? (**Show work or explain.**)

I: 7A F: 7A
I F
1) A = 1(7e-) + 4(7e-) - (1e-) = 34 val e−

2) Draw skeleton structure. The more EN F atoms attached to I. This accounts for 10 e$^-$.



Iodine is in the middle

3) Put 6 e$^-$ on each F to fulfill octet. This uses 24 e$^-$.

4) # e$^-$ left = 34 e$^-$ - (8 e$^-$ + 24 e$^-$) = 2 e$^-$
These go on the I atom. This gives 10 e- on the I atom, more than an octet.

I has 4 bonds & 1 lpe$^-$ in this case since it is in the middle (when halogens are on the outside they have only 1 bond, F is always on the outside, never in the middle)

The **ED** geometry around the I is **trigonal bipyramidal**. There are **5 electron domains** around the Br with angles of 90° and 120°.

The **molecular geometry** is **seesaw** with **bond angles** of ~ **90° and ~ 120°**. The electron pairs push the F atoms closer together so bond angles are less than or approx. 90° and 120°.

11. (6 pts) Consider the following molecules and select those that are **<u>non</u>**polar.

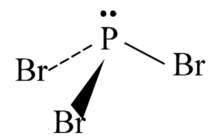
1) PBr_3 2) BH_3 3) H_2S 4) CH_2Cl_2 5) CS_2

a) 1, 2 b) 1, 3 c) 2, 4 d)* 2, 5 e) 2, 4, 5

1) PBr_3

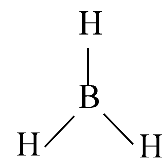
trigonal pyramidal: 4 things around P and they are not all identical (3 Br and **1 lpe$^-$**)
lpe$^-$ on P ($\approx$ 109.5° angles)

Polar (like **:**NH_3, **:**NF_3, **:**PH_3, **:**PF_3, etc.)



*2) BH_3

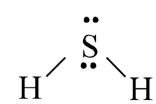
trigonal planar (120° angles, exactly)
3 things around B and **<u>all</u> identical**
(and no lpe$^-$)
Nonpolar (like BH_3, BF_3, $AlCl_3$ etc.)



3) H_2S

bent: 4 things around S and not all identical (2 H and **2 lpe$^-$**)
lpe$^-$ on O ($\approx$ 109.5° angles)

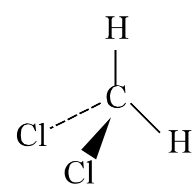
Polar (like $H_2\ddot{O}$**:**, $H_2\ddot{S}$**:**, etc.)



4) CH_2Cl_2

tetrahedral ($\approx$109.5° angles)
all 4 atoms on C are **<u>not</u>** identical

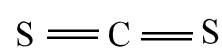
Polar (like $CHCl_3$, CH_3Cl, CH_2F_2, ect.)



*5) CS_2

linear (180° angles)
the 2 atoms on C are **identical**

Nonpolar (like CO_2)



<u>Note</u>: The symmetric shapes (linear, trigonal planar, tetrahedral, trigonal bipyramidal, octahedral and square planar) are the only ones that can give nonpolar. For linear, trigonal planar and tetrahedral all surrounding atoms have to be identical to each other for the molecule to be nonpolar.

For CH_2Cl_2 (#4) all surrounding atoms are **<u>NOT</u> identical** so the molecule is **<u>polar</u>**.

Also, the molecules (1 & 3) with **lpe$^-$** are **polar**. Generally, if there are 1 or more lpe$^-$ on the central atom, the molecule will be polar (at least for molecular shapes coming from ED geometries involving 2, 3 or 4 ED). The exceptions to this are for the linear molecular geometry arising from the trigonal bipyramidal ED geometry and the square planar molecular geometry arising from the octahedral ED geometry. These can be nonpolar if all the atoms surrounding the central atom are identical even though there are also **lpe$^-$** on the central atom.

2 & 5 are Nonpolar