

Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions. I have intentionally left a great deal of space for each problem. I do not expect each problem to take up all of the space provided!

Warmup. 4 points each

1. How many unpaired electrons are present in an oxygen atom?

- a. 0
- b. 1
- c. 2
- d. 3

Answer **C**

2. Which is the most polar bond?

- a. O-F
- b. N-F
- c. F-F
- d. C-F

Answer **D**

3. Arrange the following in terms of increasing electron affinity: K, F, P, O

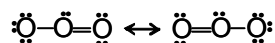
- a. $K < F < P < O$
- b. $K < P < O < F$
- c. $F < O < P < K$
- d. $P < K < O < F$

Answer **B**

4. Which of the following orbitals cannot exist according to modern quantum theory: 2s, 3p, 2d, 3f, 5p, 6p? Briefly justify your reasoning.

For an orbital to be valid, ℓ must be between 0 and $n-1$. If we recall that for $\ell = 0$ for s orbitals, $\ell = 1$ for p orbitals, $\ell = 2$ for d orbitals, and $\ell = 3$ for f orbitals then we can make some decisions. From the list above, the 2d and 3f orbitals have $n = \ell$, which violates our rule for valid quantum numbers, therefore they do not exist.

5. We can write resonance structures for ozone as shown below. What does the " \leftrightarrow " mean? Why do we sometimes need to invoke resonance?



The concept of resonance and the double headed arrow we use is an attempt to account for the fact that we cannot, by following our rules, draw an accurate Lewis structure for ozone (and many other compounds). The double headed arrow reminds us that the true structure for the compound is an average of the structures drawn and that the compound does not flip between the structures shown.

Complete all of problems 6-9.

6. Write the ground state electron configurations for the following species. You may choose to use noble gas notation if you wish. Are all of the electrons in the valence shell of each atom paired? (15 points total, 5 points each)

a. selenium



b. silicon



c. nickel (II) ion

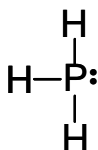


7. Complete the table for **two (2)** of the species below: (12 points)

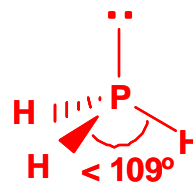
Species	Lewis Structure (indicate resonance if necessary)	Electron Pair Geometry	Molecular Geometry	Polar Molecule? (yes/no)
NO_2^-	$[\text{:}\ddot{\text{O}}\text{--}\ddot{\text{N}}\text{=}\ddot{\text{O}}\text{:}]^- \leftrightarrow [\ddot{\text{O}}\text{=}\ddot{\text{N}}\text{--}\ddot{\text{O}}\text{:}]^-$	trigonal planar	bent	yes
BrF_5		octahedral	square pyramidal	yes
CS_2	$\text{:}\ddot{\text{S}}\text{=C=}\ddot{\text{S}}\text{:}$	linear	linear	no

8. Below are the Lewis structures for two compounds. For each compound, name the molecular geometry and provide a three dimensional sketch of the compound. Indicate approximate bond angles (12 points)

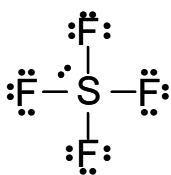
a. PH_3



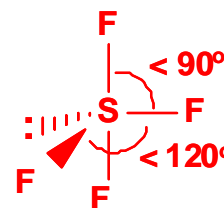
PH_3 has tetrahedral electron pair geometry, which leads to **trigonal pyramidal molecular geometry**. The presence of an unshared pair of electrons should make all of the bond angles less than the 109.5° ideal angle.



b. SF_4



SF_4 has trigonal bipyramidal electron pair geometry, which leads to **see-saw molecular geometry**. The presence of an unshared pair of electrons should make all of the bond angles less than the ideal angles of 90° for the axial atoms and 120° for the equatorial.



9. Each drawing represents a type of an atomic orbital. Give the letter designation if the orbital, its value of l , and specify the number of angular nodes (nodal surfaces). Also provide the minimum necessary value of n for an orbital of each type to exist. (12 points)

orbital diagram			
l value	2	1	0
letter designation	d	p	s
# of angular nodes	2	1	0
minimum value of n for this orbital type	3	2	1

Part II Answer two (2) of problems 10-13. Clearly mark the problems you do not want graded. 15 points each.

10. The ionization energy of an element is the minimum energy required to remove an electron from the element. The ionization energy of gold is 890.1 kJ/mol. Is light with a wavelength of 225 nm capable of supplying enough energy to ionize a gold atom? What is the maximum wavelength of light that will ionize gold?

$$\Delta E = \frac{890.1 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ atoms}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = \frac{1.479 \times 10^{-18} \text{ J}}{\text{atom}} = \frac{hc}{\lambda}$$

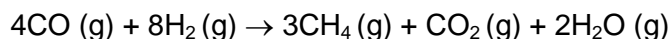
$$\lambda = \frac{hc}{\Delta E} = \frac{6.63 \times 10^{-34} \text{ Js} \times 3.00 \times 10^8 \text{ m/s}}{1.479 \times 10^{-18} \text{ J}} = 1.34 \times 10^{-7} \text{ m} = \mathbf{134 \text{ nm}}$$

Any wavelength shorter than 134 nm will possess enough energy to promote ionization. Since 225 nm is larger than 134 nm, 225 nm light is not energetic enough to ionize gold.

11. Briefly explain why the first ionization energy of Ca is greater than that of K, but the second ionization energy of Ca is lower than the second ionization energy of K.

Your discussion should focus on two issues, the importance of effective nuclear charge (Z^*), and the stability of filled valence orbitals. Considering the first ionization energy we focus on effective nuclear charge. Ca has a larger Z^* than potassium, therefore, it will be more difficult to remove an electron from calcium than potassium. Simply stating that calcium is farther right on the periodic table is not enough. Once each species has lost an electron, the stability of filled orbitals plays a larger role. Potassium ion (K^+) has a noble gas configuration, requiring the loss of a core electron in the second ionization step. This is much more energy intensive than the second ionization of calcium, which involves the loss of a valence electron.

12. Substitute natural gas (SNG) is a mixture containing methane gas that can be used as a fuel. One reaction for the production of SNG is shown below.



- a. Calculate the $\Delta H^\circ_{\text{rxn}}$ for the above process based on the table of bond dissociation energies given on the last page of this exam (12 points)

Structures	$:\text{C}\equiv\text{O}:$	$\text{H}-\text{H}$	\rightarrow	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	$\text{O}=\text{C}=\text{O}$	$\text{H}-\text{O}-\text{H}$
Bonds Broken	4(C \equiv O)	8(H-H)		--	--	--
Bonds Formed	--	--		3(4(C-H))	2(C=O)	2(2(O-H))
Energy (kJ)	4(1072)	8(436)		12(414)	2(736)	4(464)

$$\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed})$$

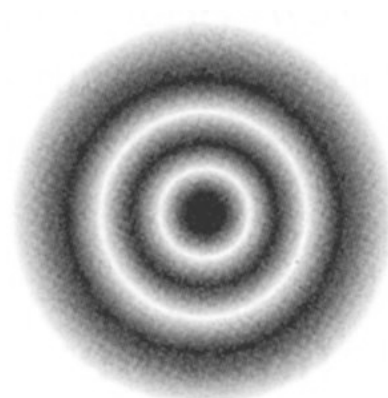
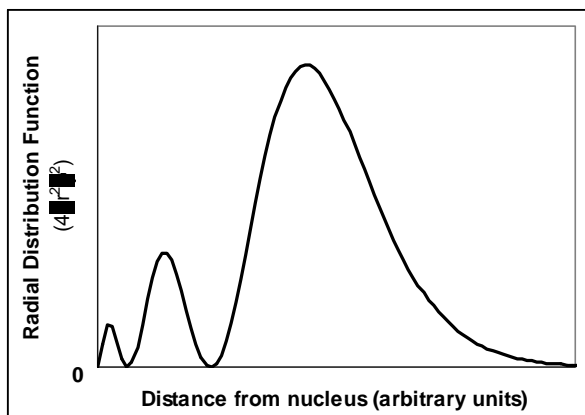
$$\Delta H = [4(1072) + 8(436)]\text{kJ} - [12(414) + 2(736) + 4(464)]\text{kJ}$$

$$\Delta H = -520 \text{ kJ}$$

- b. How should this value compare to the $\Delta H^\circ_{\text{rxn}}$ that would be determined using the standard enthalpies of formation for each of the compounds in the reaction? Justify your answer. (3 points)

Ideally, both approaches would lead to the same result, since ΔH is a state function. However, since the bond energy values are averages for several different molecules and not specific for the molecules in our reaction, we would expect some small differences in the value of the ΔH that we determine. We would expect the value to be close, but not identical.

13. Consider the following diagrams of the same orbital. Which orbital do the pictures represent? Provide the values for n , ℓ , and m_ℓ for the orbital and *justify your reasoning*.



**90% Probability Density Plot
(dark = high probability)**

To assign values for n and ℓ , we need to look for nodes in the orbitals. From the probability plot on the right, it appears that there are no angular nodes in this orbital. For this to be true, the value of ℓ must be 0, resulting in an s orbital. From the plots above, we observe 2 radial nodes in the orbital, as evidenced by the two places where the Distribution Function is zero (above right) and the two spheres of white in the Probability Density plot (above left). Therefore $n - \ell - 1$ must equal 2. If $\ell = 0$, then the value of n must be 3. With $n = 3$, and $\ell = 0$, we must have a 3s orbital. The third quantum number, m_ℓ , depends on the value of ℓ (m_ℓ ranges from $-\ell$ through zero to $+\ell$). Since $\ell=0$ for this orbital, the only possible value of m_ℓ is zero. So,

$$\begin{aligned} n &= 3 \\ \ell &= 0 \\ m_\ell &= 0 \end{aligned}$$

Possibly Useful Information

$h = 6.626 \times 10^{-34} \text{ J s}$	$c = 2.998 \times 10^8 \text{ ms}^{-1}$	$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$
$E = h\nu$	$\nu\lambda = c$	$R = 1.097 \times 10^{-7} \text{ m}^{-1}$
$H\psi = E\psi$	$\Delta E \cdot \Delta(mv) > h$	$Rhc = 2.179 \times 10^{-18} \text{ J/atom}$
$E = -\frac{Rhc}{n^2}$	$F = k \frac{Q_1 Q_2}{d^2}$	$\Delta E = -Rhc \left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right)$

Bond Dissociation Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H-H	436	C-C	347	N-N	163
H-C	414	C=C	611	N=N	418
H-N	389	C≡C	837	N≡N	946
H-O	464	C-N	305	N-O	222
H-S	368	C=N	615	N=O	590
H-F	565	C≡N	891	O-O	142
H-Cl	431	C-O	360	O=O	498
H-Br	364	C=O	736	F-F	159
H-I	297	C≡O	1072	Cl-Cl	243

1 1A																	18 8A	
1 H 1.00794	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	2 He 4.00260	
3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797	
11 Na 22.9898	12 Mg 24.3050	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B		9 9B	10 10B	11 11B	12 12B	13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9381	26 Fe 55.847	27 Co 58.9332	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80	
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.904	54 Xe 131.29	
55 Cs 132.905	56 Ba 137.327	*La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)	
87 Fr (223)	88 Ra 226.025	†Ac 227.028	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Rg (272)								

*Lanthanide series	58 Ce 140.115	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
†Actinide series	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

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