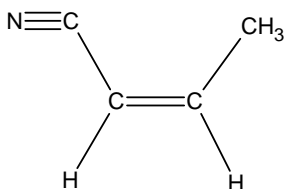


Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions.

Bonus (4 points). One day at the very beginning of class I wrote a value on the board and suggested that it be written down. Write that value here, with its correct units. _____

Complete all of problems 1-7.

1. How many sigma bonds are there in the molecule below? (4 points)



- a. 3
- b. 6
- c. 9
- d. 12

Answer c

2. A water sample is found to have 9.4 ppb of chloroform (CHCl₃). What mass of CHCl₃ would be in one glassful (250 mL) of water? (4 points)

- a. 2.35 g
- b. 2.35 mg
- c. 2.35 μg
- d. 2.35 ng

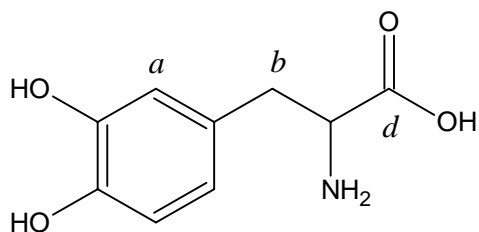
Answer c

3. In order for an ion or molecule to have square planar geometry, valence bond theory would predict that the central atom must be _____ hybridized. (4 points)

- a. sp²
- b. sp³
- c. sp³d
- d. sp³d²

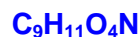
Answer d

4. For the following, consider the structure shown below of DL-Dopa, a drug often used to treat Parkinson's disease.



- I. Circle and identify three functional groups in the molecule. (6 points) **Find the amine, alcohol, and carboxylic acid groups!**

- II. What is the molecular formula for DL-Dopa? (3 points)



- III. What is the hybridization and approximate bond angles at: (6 points)

i. carbon *a*? **sp^2 , $\sim 120^\circ$ bond angle**

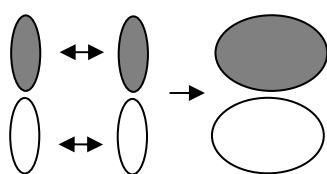
ii. carbon *b*? **sp^3 , $\sim 109.5^\circ$ bond angle**

iii. carbon *d*? **sp^2 , $\sim 120^\circ$ bond angle**

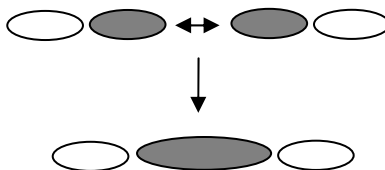
5. In the context of valence bond theory, describe how p-orbitals can form both sigma (σ) and pi (π) bonds, but s-orbitals do not. Feel free to use sketches to illustrate your points. (15 points)

The key point here is that in order to form sigma bonds, the orbital must be able to overlap with another orbital in such a way that the electron density is directly between the atoms. To form a pi bond, the overlap must be such that the electron density is off of the axis that connects the atoms. Since s orbitals are spherical, there is no way that they can overlap to form pi bonds, but because of the shape of a p-orbital, there is the possibility of both end-to-end (sigma bond) and side-to-side (pi bond) overlap.

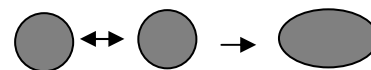
p-orbital overlap to form pi bond



p-orbital overlap to form sigma bond



s-orbital overlap to form sigma bond



6. More complex theories must be developed to deal with the shortcomings of more basic theories. Shortcomings of valence bond theory are highlighted by the two experimental observations below. For **one** of the observations, clearly describe how molecular orbital theory can account for the observation. (15 points)
- Molecular oxygen (O_2) is paramagnetic.
 - Ozone (O_3) has only one type of O-O bond, not one single and one double bond.

The key limitation of valence bond theory is that it still considers two electrons shared between two atoms as a bond. This causes problems for both considerations. In your discussion for the observations, you should address the following points:

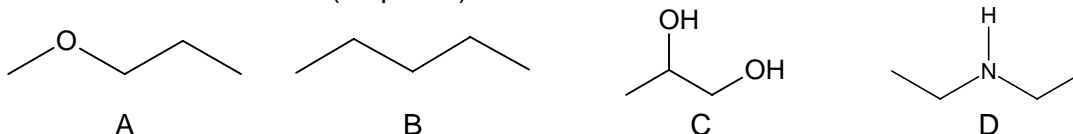
For observation (a):

- For O_2 to be paramagnetic, the model must account for unpaired electrons
- MO's, like atomic orbitals, can hold up to two electrons, and can be filled, unfilled, or half-filled.
- In O_2 , the arrangement (energies) and number of electrons are such that at least one (actually two) of the MO's are half-filled.

For observation (b):

- For ozone to have only one type of bond, we cannot limit the model to "two electrons between two atoms is a bond".
- We consider MO's to describe the electron density across an entire molecule.
- Therefore, it becomes possible to model the bonding in O_3 as a result of delocalizing electrons across the entire molecule, resulting in the observed bond order and bonding characteristics.

7. Consider the compounds below. Remembering that "*like dissolves like*," arrange the molecules in order of increasing solubility in water. Clearly justify your reasoning. Ignore any effects of molecular mass. (15 points)



Your order and justification should be based in the types of intermolecular forces each of the compounds is capable of participating in, **relative to those of water**. Since water is polar and undergoes hydrogen bonding; polar, hydrogen bonding compounds will be more soluble than nonpolar compounds. In order of increasing solubility: $B < A < D < C$

B: nonpolar, only dispersion forces

A: somewhat polar, but not capable of participating in H-bonding

D: polar, capable of H-bonding (amine)

C: polar, capable of H-bonding (alcohol). Stronger tendency for H-bonding than D because of more polar O-H bond (compared to N-H)

Part II Answer two (2) of problems 8-11. Clearly mark the problems you do not want graded. 15 points each.

8. A forensic chemist is given a white solid that is expected of being pure cocaine ($C_{17}H_{21}NO_4$, 303.36 g/mol). She dissolves 1.22 g of the solid in 15.60 g of benzene ($K_b = 2.53^\circ\text{C kg/mol}$, $K_f = 5.12^\circ\text{C kg/mol}$). The freezing point is lowered by 1.32°C . Assuming a 1% uncertainty in her measurements, can the chemist state that the substance is likely to be cocaine?

Based on the freezing point depression, we should be able to determine the molality, and ultimately the molar mass of the solid:

$$\Delta T = K_{fp}m \quad \text{or} \quad m = \frac{\Delta T}{K_{fp}} = \frac{1.32^\circ\text{C}}{5.12^\circ\text{C kg/mol}} = \frac{0.2578 \text{ mol}}{\text{kg benzene}}$$

So, with this concentration, what must the molar mass of the solute be?

$$\frac{0.2578 \text{ mol}}{\text{kg benzene}} \times 15.6 \text{ g benzene} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.004022 \text{ mol compound}$$

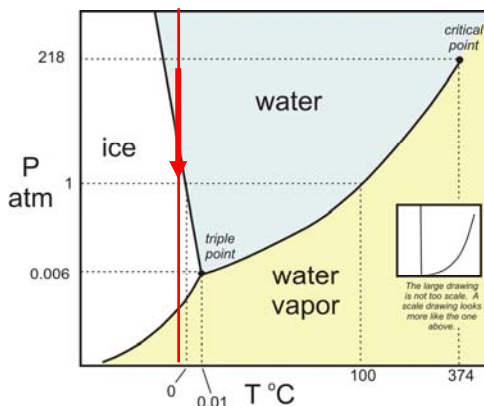
And the molar mass is:

$$\frac{1.22 \text{ g}}{0.004022 \text{ mol}} = 303.3 \text{ g/mol}$$

This molar mass correlates well with that of cocaine, supporting identification.

9. You decide to cool a can of soda (or pop depending on where you are from) quickly by placing it in the freezer. When you take the can out, the contents are still liquid, but when you open the can, the soda (or pop) immediately freezes. Explain why this happens. A phase diagram for water is shown below.

Since the majority of the solution is water, the water phase diagram is a good approximation of the phase behavior of the soda. Consider the red line added to the phase diagram. This line corresponds to 0°C , the temperature at which water freezes at 1 atmosphere. In a freezer, the temperature would be somewhere less than 0°C , so we would be somewhere to the left of this line. Since soda (or pop) is under pressure, yet the contents are still liquid in the unopened can, we must be operating in the "water" region to the left of the red line (we would say that the solution is "supercooled"). When we open the can, we release the pressure (it returns to atmospheric pressure), but the temperature remains unchanged, therefore the system will undergo a phase change corresponding to the red arrow in the diagram (a liquid to solid change), and the solution freezes.



10. The atomic radius of tungsten, W, is 202 pm. If the density of W is 19.3 g/cm³, does tungsten form a face-centered cubic lattice? Justify your answer.

Let's start by assuming W is fcc. If so, what would its density be? Based on our knowledge of the fcc structure, the length of a diagonal of one face is 4(radius of the atom). Knowing this, we can find the volume of a unit cell.

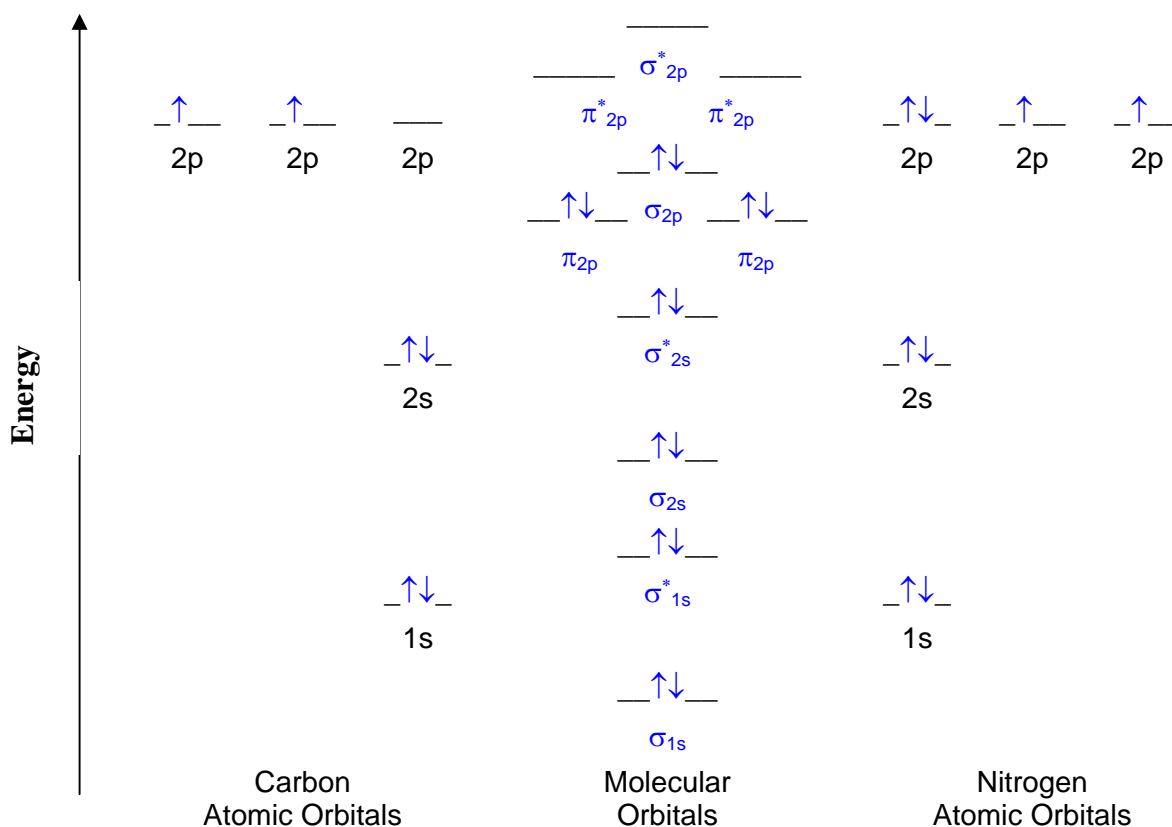
$$a^2 + a^2 = [4(202\text{pm})]^2, \text{ so } a = 571 \text{ pm and } a^3 = \text{volume of unit cell} = (571 \times 10^{-10} \text{ cm})^3$$

$$\frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{1 \text{ unit cell}}{1.865 \times 10^{-22} \text{ cm}^3} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ atoms}} \times \frac{183.85 \text{ g}}{1 \text{ mol}} = \frac{6.55 \text{ g}}{\text{cm}^3}$$

So, if W were fcc, we'd expect a density of 6.55 g/cm³, since the reported density is 19.3 g/cm³, W must not form a face-centered cubic lattice.

11. Answer the following questions regarding the CN⁻ ion:

- a. Complete and clearly label the molecular orbital diagram for CN⁻, whose molecular orbital energy levels are similar to those in N₂. Fill MO's with electrons as appropriate. For this problem, we will ignore any differences in the energies of the atomic orbitals in nitrogen as compared to carbon. (9 points) **14 electrons total!!! (C-6, N-7, (-)-1)**



- b. Is CN⁻ paramagnetic? Justify your response. (3 points)
 Since CN⁻ has no unpaired electrons, it is diamagnetic
- c. What is the bond order in CN⁻? Show how you arrived at your answer. (3 points)
 Bond Order = (10 bonding electrons – 4 antibonding electrons)/2 = 3

Possibly Useful Information

$$R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$a^2 + b^2 = c^2$$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$\Delta t_{fp} = k_{fp} m$$

$$\Delta t_{bp} = k_{bp} m$$

$$\Pi = MRT$$

$$P_{\text{soln}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$$

Selected Constants

Solvent	Boiling Point (°C)	K_b (°C kg/mol)	Freezing Point (°C)	K_f (°C kg/mol)
Water	100.0	0.51	0	1.86
Benzene	80.1	2.53	5.5	5.12
Ethyl Ether	34.5	2.02	-116.2	1.79
Chloroform	61.2	3.63	-63.5	4.70

1 1A																				18 8A							
1 H 1.00794	2 2A																				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	3B	4B	5B	6B	7B	8B	9	10	11 1B	12 2B	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	57 *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	89 †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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