Q1) 12 points (2 points each)

Arrange the following (Use ">" or "<" to show decreasing and increasing order, respectively. If two options have the same value, use "=" between them)

a) **Decreasing** order of wavelength of a photon for the following transitions in a H atom (assume all given transitions are possible):

2s to 3p

3d to 2p

1s to 3p

2p to 1s

3d to 1s

2s to 3p = 3d to 2p > 2p to 1s > 1s to 3p = 3d to 1s

b) **Increasing** boiling point:

Hexane;

2,3-dimethylbutane; 2-methylpropane; CH₃CH₂CH₂CH₂CH₂CH₂OH

2-methylpropane < 2,3-dimethylbutane < Hexane < CH₃CH₂CH₂CH₂CH₂CH₂OH

c) **<u>Decreasing</u>** number *delocalized* electrons

Benzene

 O_3

 CO_2

HCOO-

Benzene (6) $> O_3 = HCOO^-$ (4 for both) $> CO_2$

Also accepted: Benzene (6) $> O_3 = HCOO^- = CO_2$ (4 for all)

d) **Increasing** number of *unpaired* electrons

 Mo^{2+}

 Zn^{2+}

 Fe^{3+}

 Zr^{2+}

 $Zn^{2+} < Zr^{2+} < Mo^{2+} < Fe^{3+}$

e) **Decreasing** size

 Cs^+

 Sr^{2+}

Ţ-

 Mg^{2+}

 $I^- > Cs^+ > Sr^{2+} > Mg^{2+}$

f) **Increasing** number of valence electrons

F

In

Mn

Ru

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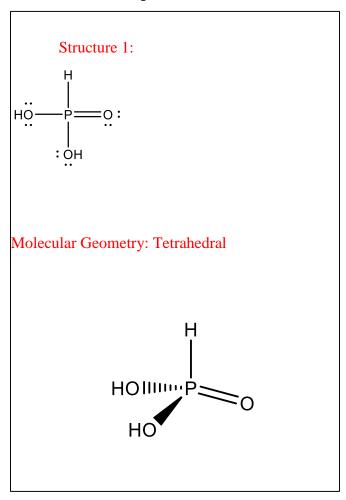
In < F = Mn < Ru

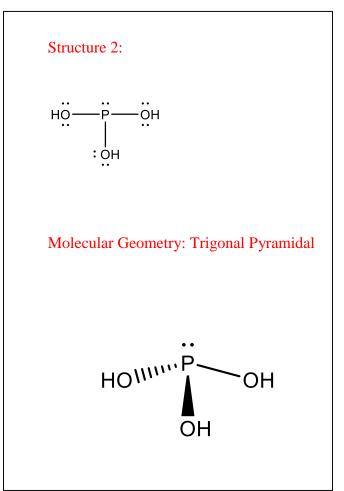
NO PARTIAL MARKS AWARDED FOR ABOVE

Q2) 9 points

There are two possible ways to draw the Lewis structure of H_3PO_3 in both of which all of the atoms have zero formal charge, but each have <u>different molecular geometry</u> at the central atom (P).

a) Draw both Lewis structures for H₃PO₃ (<u>there are no O-O bonds</u>). Indicate and draw (show solid wedge-dashed bonds) the molecular geometry around phosphorous atom for both the Lewis structures. **8 points**





b) Are these Lewis structures resonance structures of each other? Why or why not? 1 points

No, these are not resonance structures. There is rearrangement of atoms in the two structures above

Q3) 8 points

The **ionization energy (in kJ/mol)** for a given period 2 element are the following:

	IE_1	IE_2	IE ₃	IE ₄	IE ₅	IE_6	IE ₇	IE_8
X	1314	3388	5296	7467	10987	13320	71320	84070

a) What is element X? Briefly explain your reasoning. **3 points**

X is oxygen. Change from IE₆ to IE₇ is the largest change. Removal of the 7^{th} electron must be removal of an electron from an ion with noble gas configuration (i.e there are 6 valence electron). X^{6+} is noble gas configuration: oxygen

b) Using the ionization energy values given above, calculate the **lowest frequency** (3 sig. figures) of a photon that can remove an electron from the ground state atom X? Show calculations. **5 points**

Lowest frequency = lowest energy = 1314 kJ/mol

Convert kJ/mol to J to get energy of one photon $= 1314 \text{ kJ/mol} * 1000 \text{ J/kJ} * 1 \text{mol/} 6.023 \text{ x } 10^{23} = 2.18 \text{ x } 10^{-18} \text{ J}$

 $E = h \nu$

 $\nu = E/h = 2.18 \ x \ 10^{\text{-}18} \ J \ / \ 6.626 \ x \ 10^{\text{-}34} \ J.s = 3.29 \ x \ 10^{15} \ s^{\text{-}1}$

Answer: 3.29 x 10¹⁵ s⁻¹

Q4) 11 points

a) A photon of wavelength 300 nm strikes an electron in a metal. The work function of the metal is $3.5 \times 10^{-19} \text{ J}$. What is the velocity (ms⁻¹; 2 significant figures) of the electron ejected, assuming it was initially at rest? Show calculations. **7 points**

$$E_{photon} = hc/\lambda = 6.626 \text{ x } 10\text{-}34 \text{ Js} * 2.998 * 10^8 \text{ ms}^{-1} / (300 * 10^{-9} \text{ m})$$

$$E_{photon} = 6.626 \times 10^{-19} J$$

From photoelectric effect equation:

$$E_{photon} = work \; function + KE_{electron}$$

$$6.626 \times 10^{-19} = 3.5 \times 10^{-19} + KE$$

$$KE = 3.126 \times 10^{-19} J$$

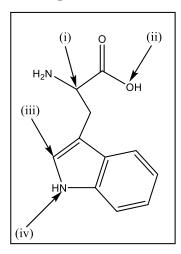
$$KE = \frac{1}{2} mv^2$$

$$v = (2KE / m)^{1/2}$$

$$v = 8.3 \times 10^5 \text{ ms}^{-1}$$

- b) Without doing any calculations, predict the change (increase, decrease, or no change) for the following, if the wavelength of the photon was changed to 200 nm. **4 points**
 - 1. Work function of the metal: No change
 - 2. Velocity of the electron: Increase
 - 3. Number of electrons ejected: No change
 - 4. Kinetic energy of the electron: Increase





For the indicated atoms (denoted with an arrow), (i) to (iv), answer the following questions. Lone pairs are **not** indicated in the structure. All atoms have formal charge of 0.

a) (2 points) Describe the orbitals involved in all bonds formed by C(i). Designate sigma and pi bonds.

2 sp³-sp³ sigma; sp³-s sigma; sp³-sp² sigma

b) For (ii)

1. **(1 point)** Indicate the <u>molecular geometry</u> at O:

Bent

2. (1 point) Circle the one value that best describes the C-O-H bond angle.

>90° to <109.5°

109.5°

>109.5° to <120°

120°

>120° to <180

c) For (iii)

1. **(1 points)** Indicate the **hybridization** at C(iii): sp²

2. (3 points) Consider x as the bond axis, how many p_x - p_x and p_y - p_y pi bonds does (iii) have?

 p_x - p_x pi bonds = $\boxed{ 0 \text{ or } 1 }$

d) For (iv)

1. (1 point) Indicate the molecular geometry at (iv): trigonal pyramidal

2. (1 point) Circle the one value that best describes the H-N-C bond angle.

>90° to <109.5°

109.5°

>109.5° to <120°

120°

>120° to <180

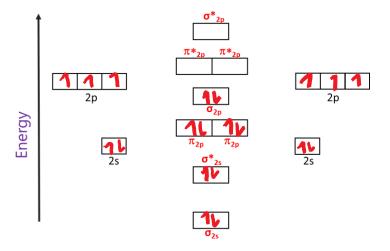
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Q6) 10 points

a) Draw the molecular orbital (MO) diagram for N₂ (valence orbitals only). Label all the atomic and molecular orbitals (No need to show contribution/dotted lines from atomic orbitals). What is the bond order for N₂? **6 points**



Bond order for $N_2 = 3$

- b) Based on MO diagrams only, predict which of the following has the higher ionization energy (IE) in each case, and why? **4 points**
 - 1. Higher IE: N_2 or N_2^{2-} N_2 has a higher IE than N_2^{2-} as electron being removed from a more stable orbital
 - Higher IE: C₂ or C₂²⁻
 C₂ has a higher IE than C₂²⁻ as electron being removed from a more stable orbital

Answer incomplete/incorrect if explained in terms of magnetism or bond order.

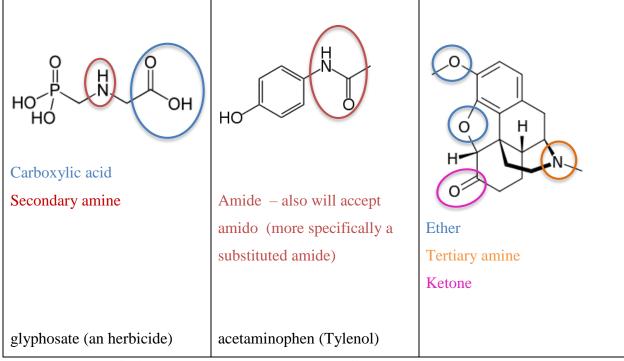
Q7) 11 points

- a) Carbon can form bonds with itself as well as other elements. **5 points**
 - i. In addition to the halogens, what 5 other atoms most *commonly* bond to carbon in organic compounds? (symbols or names are accepted)

H, O, N, P, S (part marks)

- ii. Which of those 5 atoms in part *i* are heteroatoms?
 - O, N, P, S –(also accepted) or all except H (no part marks)
- iii. From the 5 atoms in part i, which elements are more electronegative than carbon?O, N (no part marks)
- iv. From the 5 atoms in part *i*, which elements are less electronegative than carbon?

 H, P (no part marks)
- b) Circle and name the type of functional groups in each compound below. Specify if each is primary, secondary, or tertiary. **6 points**



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		hydrocodone
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Q8) 17 points

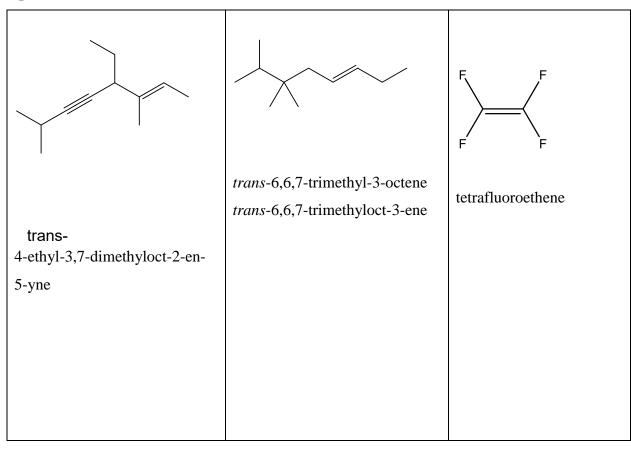
a) Draw the following structures in the space provided. 3 points

b) Circle any problems with the structures drawn below and draw the *corrected* structures as carbon skeletons. **6 points**

Question 8 continued on next page

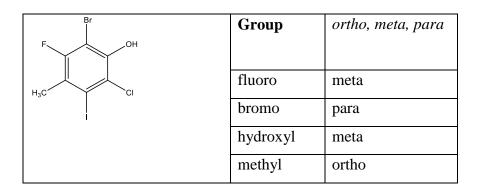
c) Provide the correct IUPAC names for the following structures. If necessary, specify cis vs trans.

6 points



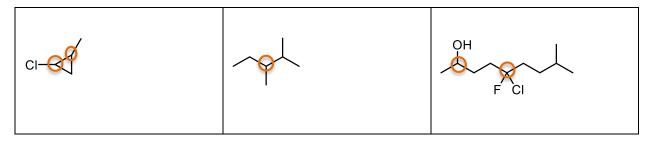
d) Taking the iodo as your reference, indicate the position of the other substituents as ortho, meta, para.

2 points



Q9) 12 points

a) Circle all the chiral centres in the structures below. **3 points** (no part marks)

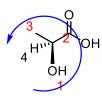


b) Give each molecule the appropriate stereochemical assignment (R vs S). Explain the steps you use to assign R vs S. 6 points



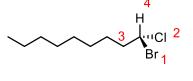
S

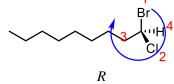
- -Label all groups in terms of priority.
- -Lowest priority (4, the methyl) is already pointing to the back.
- -Draw an arrow from highest to lower priority.
- -It is counterclockwise, so *S*.



S

- -Label all groups in terms of priority.
- -Lowest priority (4, the previously hidden H) is already pointing to the back.
- -Draw an arrow from highest to lower priority (1 to 3).
- -It is counterclockwise, so *S*.





- -Label all groups in terms of priority.
- -The lowest priority (4, the H) must point to the back. So redraw so that the H is in the back. -Now, with the redrawn structure, draw an arrow from highest to lower priority (1 to 3). It is clockwise, so *R*.
- c) Draw the Newman projection of the molecule below in the box provided, from the perspective indicated. **3 points**



Q10) 11 points

a) What is the definition of a nucleophile? 1 point

An "electron" rich species. (seeks a positive centre) (no part marks)

b) Circle the stronger nucleophile in each pair, and explain why it is a stronger nucleophile. 6 points

Nucleophiles	Reason
H ₂ O vsOH	
	Negatively charged nucleophile is stronger than its conjugate acid
Br vs F	Br- is larger than F-, so electrons are more loosely held when comparing
	down a group. (also accepted: Br- is more polarizable)
NH ₂ vs NH ₃	
	Negatively charged nucleophile is stronger than its conjugate acid
CH ₃ -vs NH ₂ -	
	Carbon is less electronegative, more polarizable. (also accepted: basicity
	increase from right to left across the same row)

c) Label each reaction event below with either the bonding-breaking type or the specific reaction type.

Choose the type that **best** describes the reaction event drawn. **4 points** (no part marks)

Choices: substitution, addition, elimination, rearrangement, heterolytic cleavage, homolytic cleavage

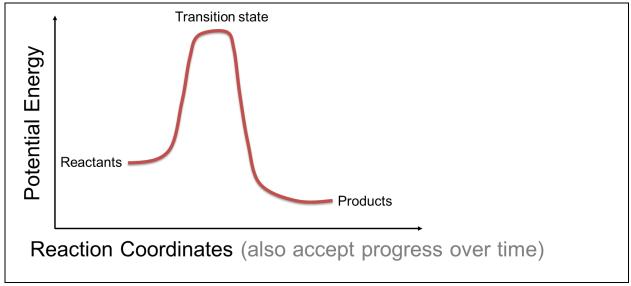
Reaction scheme	Reaction type (one best choice)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Substitution
: Ċ!	Homolytic cleavage
+ HCN → OH CN	Addition reaction
+ CI + H ₂ O	Elimination

Q11) Draw the products of the reactions (carbon skeleton). 8 points

Q12) 10 points

a) Draw a reaction energy diagram for a concerted, exothermic reaction. Include all the necessary labels.

5 points



b) Complete the S_N2 reaction below. If there is a key intermediate or transition state, be sure to draw this and label if it is a transition state or an intermediate. Draw the curved arrows to show the movement of electrons (making and breaking bonds). **5 points**

$$: \overrightarrow{OH} + H - \overrightarrow{C} - \overrightarrow{Br}: \rightarrow Br: \rightarrow Br: \rightarrow Br: \rightarrow H_3C - \overrightarrow{OH}$$
transition state

Q13) 8 points

a) What is the coordination number of the complex and oxidation state of the transition metal in the following coordination complexes? **6 points** (no part marks)

Coordination complex	Oxidation state	Coordination number
[Co(en) ₂ Cl ₂]OH	+3 (overall charge of the complex is + 1 since the complex interacts with -1 hydroxyl)	6 (note en is a bidentate ligand1)
Br., NH ₃ H ₃ N Br	+ 2 (the overall complex is neutral so 2 bromines of negative charge balance with a +2 Pt charge)	4
tetraamminebromochloroplatinum(IV) chloride	+4 (it says in the name!)	6

b) In $[Cr(OH)_6]^{3-}$, is the chromium ion diamagnetic or paramagnetic? Show the electron configuration to explain why chromium is either diamagnetic or paramagnetic. **2 points**

Paramagnetic.

Electron configuration of $Cr = [Ar] 4s^1 3d^5$

Cr in this complex = oxidation state 3+

Electron configuration of $Cr3+ = [Ar] 3d^3$

→ These 3 electrons are unpaired and therefore are paramagnetic

Q14) 8 points

a) Provide the systematic name for the following two coordination compounds. 2 points (no part marks)

 $[Zn(H_2O)Cl(en)_2]Br$

Potassium hexacyanoferrate(II)

aquachlorobis(ethylenediamine)zinc(II) bromide

b) If any of the following complexes can exist as isomers, state the type of isomerism and draw the structures. **6 points**

$[Zn(en)F_2]$

not isomers

[Zn(H₂O)(NH₃)FCl]

This is a tetrahedral complex, and there are four different ligands – so it's like a "chiral center". As such, we see enantiomers.

$[PtCl_2Br_2]^{2\text{-}} \ (square \ planar)$

since this is square planar we

can have geometric

(cis/trans)isomers

Q15) 5 points

a) In each set of coordination complexes, circle which coordinate complex has the largest crystal field splitting energy. **2 points** (no part marks)

i.		ii.
Coordination	Maximum absorbance	
complex	λ	$[Ti(NH_3)_6]^{3+}$
$[Fe(A)_6]^{3+}$	700 nm	[TiF ₆] ³⁻
$[{\rm Ti}({\rm A})_6]^{3+}$	510 nm	$[\mathrm{Ti}(\mathrm{CN})_6]^3$
$[Cr(B)_{6}]^{3-}$	400 nm	$[{\rm Ti}({\rm H_2O})_6]^{3+}$
$[Fe(B)_6]^{3-}$	305 nm	

b) Why is the +2 oxidation state so common among transition elements? 1 point

The outermost (ns2) electrons are easily lost, producing the +2 oxidation state. (simply saying because the s electrons are easily lost is fine too)

c) How does the variation in atomic size across a transition series contrast with the variation across the main group elements of the same period? Briefly explain why there is a difference for the transition series. **2 points**

For the main-group elements, size decreases as you move to the right. For the transition elements, the size decreases at first and then is fairly constant since inner orbitals are being filled.