Section 1.01 Instructions:

Answer 4 questions.

Answer one question from each of Sections A and B and two questions from Section C.
Section A

Answer one question from this section.

1. Answer each of the following:

Discuss the chemistry of oxygen and iron in biological systems. In your answer pay particular attention to the following:

(a) The roles of iron and oxygen in biology [20 marks]
(b) Iron containing enzymes and the reactions they catalyse [20 marks]
(c) The reduction of oxygen in biological systems [30 marks]
(d) Iron-oxygen intermediates in catalytic pathways [30 marks]

2. Answer each of the following:

(a) For the following complexes, give the valence electron count and the formal oxidation state of the metal. In each case show how you have reached your conclusion.

(b) As part of a project to evaluate the properties of phosphine ligands a student makes a series of complexes of the general formula \( \text{(CO)}_5W(PX_3) \) (\( X=\text{Alkyl, Aryl} \)). How could they easily estimate the relative electron donor power of the various phosphine ligands? Explain your answer. [25 marks]

(c) Explain the factors which effect the characteristics of the P-X bond in a complex such as \( \text{(CO)}_5W(PX_3) \) where \( X=\text{OPh} \). [20 marks]

(d) The compound \( \text{Cp}_2\text{Ti(\eta}^2\text{-Me}_2\text{SiCCSiMe}_2) \) has an interesting structure. The C-C bond in the co-ordinated alkyne measures an unusually long 1.283Å and the C-C-Si angles are 146° and 148°. Explain these structural features with respect to the bonding of alkynes to metal atoms. Draw the orbitals involved in each facet of the bonding. [37 marks]

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3. Answer each of the following:

(a) (i) Explain the "molecular library approach" for the construction of molecular polyhedra using a cube as an example. Give one specific example for a metal complex and a ligand that will self-assemble into a cube and comment on the reaction conditions required. [25 marks]

(ii) Explain the thermodynamic and kinetic stability of molecular cubes. [10 marks]

(b) Briefly discuss why the design of synthetic receptors that recognize and bind anions with high affinity in water is challenging. [30 marks]

(c) Comment on the following plot of stability constants vs. group I cation. Suggest a crown ether that would give a higher logK value for Li⁺ than the three crown ethers shown in the plot. Give a reason for your choice. [35 marks]

4. Answer each of the following:

(a) (i) Explain what is meant by the term *decomposing precursor* in solid state synthesis. Use the *decomposing precursor* synthesis of BaTiO₃ along with relevant reaction schemes to aid your answer. [15 marks]

(ii) Give an alternative synthetic route to BaTiO₃ (not employing the *decomposing precursor* route), highlighting why it may not be the most effective synthetic route. [15 marks]

(iii) BaTiO₃ has many structural analogues. Give the name of these types of compounds and give two other known examples. [5 marks]

Question 4 continued on next page
(iv) Briefly explain what is meant by the term “doping”. Using the examples below explain why these procedures are important to solid state material chemists and engineers.
(a) Ca$^{2+}$ doped into La$_2$CuO$_4$
(b) Li$^+$ doped into CoO$_2$  

(b) The diagram below details the ionic conductivity of ‘pure’ NaCl as a function of temperature.

(i) Why is it that even the purest of NaCl can exhibit ionic conductivity?  

(ii) There are two mechanisms whereby ionic conductivity can occur in a solid. Describe both mechanisms using an illustration in each case.  

(iii) Explain briefly why ionic conductivity increases with increasing temperature. Use the figure above to aid your answer.  

(iv) Explain the nature of the ionic conductivity curve (above), highlighting the intrinsic and extrinsic regions. What information can we glean from the slope of this curve?

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Section C
Answer two questions from this section.

5. Answer each of the following:

The ligand shown below is mixed with NaCl in deuterated DMSO. Assume that a 1:1 anion-receptor complex forms and that the exchange between the receptor and the anion-receptor complex is rapid on the NMR time scale.

(a) Plot the chemical shift of the amide protons vs. the chloride concentration. Explain your workings. [22 marks]

(b) Plot the chemical shift of the amide protons vs. \([R]/([R] + [Cl^-])\) (\(R\) = concentration of the receptor) Explain the significance of the plot. [25 marks]

(c) What class of ligand does the receptor belong to? [3 marks]

6. Answer each of the following:

MgAl_2O_4 is the founder member of the ‘spinel’ class of minerals of general formula AB_2O_4.

(a) MgAl_2O_4 can be synthesised using two different routes. Describe both synthetic routes detailing advantages and disadvantages to both techniques. Discuss all starting materials associated with both MgAl_2O_4 synthetic routes. Use reaction schemes and illustration(s) to aid your answer. [40 marks]

(b) Give plausible starting materials (A, B, C and D), reagents and conditions for the successful synthesis of the following:

\[ A + B \rightarrow \text{SiO}_2 \] [5 marks]
\[ C + D \rightarrow \text{Li}_x\text{CoO}_2 \] [5 marks]

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7. Answer each of the following:

Read the following paragraph taken from the literature\#. Answer the questions that follow.

“A high valent intermediate has not yet been unequivocally observed in the catalytic cycle of cytochrome P450, but there is strong indirect evidence for its involvement. First, Fe(III)-cytochrome P450 can react with peroxides and oxygen atom donors such as C_6H_5IO and ClO\(^-\) to generate species capable of performing the same reactions as the native enzyme. This reaction bypasses the Fe(II) oxidation state in the P450 cycle and is known as the peroxide shunt. Second, related heme peroxidases react with \(\text{H}_2\text{O}_2\) to afford a transient high-valent intermediate called Compound I. Compound I is formally Fe\(^V\)=O, but has been spectroscopically characterised for horseradish peroxidase (HRP) as an oxoiron(IV) porphyrin radical complex.”


(a) Draw a structure for Compound I. [20 marks]
(b) Give your understanding of the chemistry described in this paragraph. [20 marks]
(c) Relate the chemistry described here to the wider context of monoxygenase chemistry and biology. [10 marks]

8. Answer each of the following:

When enantiomerically pure chloride A is treated with \([\text{Fe(CO)}_4]^{2-}\) followed by carbon monoxide and then methyl iodide the organic product formed is B (in 99% enantiomeric excess).

\[
\begin{align*}
\text{Cl} & \quad \text{A} \\
\end{align*} \\
\text{B}
\]

(a) Draw the structures of all inorganic intermediates along the reaction pathway. [20 marks]
(b) In each case label the reaction type leading to the intermediates. [10 marks]
(c) What is the mechanistic implication, for the first step of the reaction sequence, of the fact that it is overall enantiospecific? [10 marks]
(d) In the complex formed after the first step of the mechanism one may envisage an unwanted reaction pathway in the absence of carbon monoxide. What is the product and how might it be formed? [10 marks]

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9. Answer each of the following:

From the information in the scheme above answer the following:

(a) What reagent A should be used in the Heck coupling? [7 marks]

(b) What is the product B? [7 marks]

(c) What reagents can be used to form the epoxide in an enantioselective manner? Give a brief explanation as to how this enantioselectivity is achieved. [15 marks]

(d) What is the product D? [7 marks]

(e) What are the two most likely products E and F? Explain why these are likely to be formed. [14 marks]