



MACHAKOS UNIVERSITY
SCHOOL OF PURE AND APPLIED SCIENCES
UNIVERSITY EXAMINATIONS 2019/2020
FIRST YEAR FIRST SEMESTER EXAMINATION FOR THE DEGREE OF
MASTER OF SCIENCE (CHEMISTRY)
SCH 802: ADVANCED COORDINATION CHEMISTRY

DATE: DECEMBER, 2019

TIME: 2 HOURS

INSTRUCTIONS:

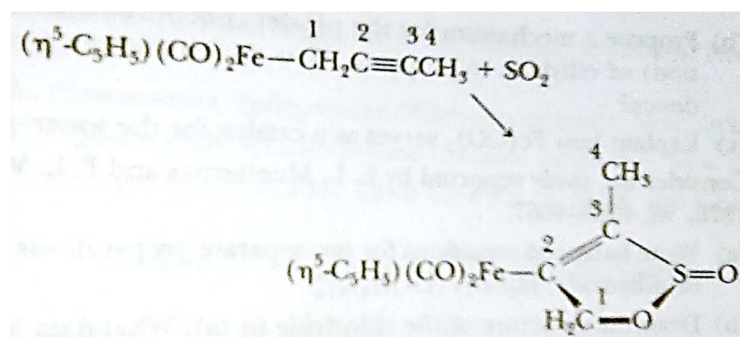
ANSWER YOUR QUESTIONS IN ANSWER BOOKLET PROVIDED.

ANSWER QUESTION ONE [COMPULSORY] AND ANY OTHER TWO QUESTIONS.

QUESTION ONE (THIRTY MARKS)

- a) State THREE applications of macrocyclic coordination (3 marks)
- b) What are the principal sets of equilibrium constants for expressing the formation of a series of complexes ML , ML_2 , ML_3 and so on? How are they related? (4 marks)
- c) Alkenes with conjugated double bonds can form independent linkages to metal atoms. Give THREE examples to illustrate this phenomenon. (3 marks)
- d) Define the following terms, giving relevant examples of each (4 marks)
 - i. Chelate
 - ii. Tetragonal distortion
- e) What is an insertion reaction? (2 marks)
- f) With relevant examples show how the following types of insertion reactions occur
 - i. 1,1-insertion
 - ii. 1,2-insertion (4 marks)

- g) Write equations for a 2-step preparation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}$ from C_5H_6 , Na, and NiCl_2 . (2 marks)
- h) Write a balanced equation showing the overall reaction in each of the following processes: the Ziegler-Natta process and the Wacker process; for the synthesis of acetaldehyde (2 marks)
- i) Suggest a mechanism for the following 1,3 insertion reactions (3 marks)



- j) What is the structure of the redox centre of the HiPIP and of the 4-Fe and 8-Fe ferredoxins? (3 marks)

QUESTION TWO (15 MARKS)

- a) Big cats such as the cheetah run at superspeed (up to 120 km/h) and have high levels of myoglobin. Explain why this is so. How do the functions of myoglobin differ from those of hemoglobin? What are the principal similarities and differences in their structures? (6 marks)
- b) Describe each of the following processes
- Hydroformylation
 - Ziegler-Natta polymerization
 - Fischer Tropsch synthesis of hydrocarbons
- (9 marks)

QUESTION THREE (15 MARKS)

- a) With relevant equations, describe any FOUR methods of synthesizing metal carbonyls (8 marks)
- b) Isotope labelling experiments and IR analysis have shown that the insertion of CO into a M-alkyl to form a metal acyl takes place by migration of the methyl group via a *cis*-coordinated CO rather than mere insertion of the CO into the metal-alkyl bond. Discuss these two phenomena, clearly detailing the mechanisms involved at each stage. (7 marks)

QUESTION FOUR (15 MARKS)

- a) Discuss the catalytic oxidation of ethylene by $\text{Pd}^{\text{II}}\text{-Cu}^{\text{II}}$ solutions. Clearly outline the mechanisms involved. (10 marks)

- b) Draw the structure of Ferrocene. Describe FOUR routes through which this compound can be synthesized (5 marks)

QUESTION FIVE (15 MARKS)

- a) Draw the structure of a porphine and explain how heme and chlorophyll are related to it. (9 marks)
- b) Graphically, with relevant equilibrium equations, distinguish between the affinities of myoglobin and haemoglobin towards oxygen (6 marks)