

UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2015/2016

TITLE OF PAPER: **ADVANCED** **INORGANIC**
 CHEMISTRY

COURSE NUMBER: **C401**

TIME ALLOWED: **THREE (3) HOURS**

INSTRUCTIONS: **THERE ARE SIX (6) QUESTIONS.**
 ANSWER ANY FOUR (4) QUESTIONS.
 EACH QUESTION IS WORTH 25
 MARKS.

A PERIODIC TABLE HAS BEEN PROVIDED WITH THIS EXAMINATION PAPER.

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QUESTION ONE

- (a) Give examples of each of the following reaction types:
- (i) A reaction of a metal with an organic halide;
 - (ii) Transmetallation;
 - (iii) Metathesis. [3]
- (b) Show with drawings the expected structures of the following cyclooctatetraene (cot) complexes:
- (i) (cot)Cr(CO)₃;
 - (ii) (cot)Fe(CO)₃;
 - (iii) (cot)PtCl₂. [3]
- (c) Predict the products of the following reactions:
- (i) $\text{Os}(\eta^5\text{-C}_5\text{H}_5)_2 + \text{CH}_3\text{C(O)Cl} \rightarrow$
 - (ii) ${}^n\text{BuLi} + \text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2 \rightarrow$
 - (iii) $(\text{OC})_5\text{Mn-Mn}(\text{CO})_5 + \text{Br} \rightarrow$ [3]
- (d) Suggest reasonable syntheses for
- (i) $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3$ starting with CrCl_3 , CO , Al and C_6H_6 ;
 - (ii) $\text{H}_3\text{C-Re}(\text{CO})_5$ using Re_2O_7 , CO , Na and CH_3I as the primary starting materials. [10]
- (e) Discuss each of the following observations:
- (i) The symmetric CO stretching frequencies in $[\text{V}(\text{CO})_6]^-$, $[\text{Cr}(\text{CO})_6]$ and $[\text{Mn}(\text{CO})_6]^+$ are 1858, 2000 and 2095 cm^{-1} respectively;
 - (ii) When CO becomes coordinated to BH_3 its stretching frequency increases, but when CO becomes coordinated to $\text{Ni}(\text{CO})_3$ its stretching frequency decreases. [6]

QUESTION TWO

- (a) Using silicon and chloromethane as the primary starting materials, give equations for the synthesis of hexamethyldisiloxane. [6]
- (b) Based on isolobal analogies, choose the group that might replace the group underlined in
- (i) $\text{Co}_3(\text{CO})_9\underline{\text{CH}}$ OCH₃, N(CH₃)₂, or SiCH₃
- (ii) $(\text{OC})_5\underline{\text{MnMn}}(\text{CO})_5$ I, CH₂, or CCH₃ [4]
- (c) Use Wade's rules to predict the structures of the following:
- (i) $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$; (ii) Os₇(CO)₂₁. [4]
- (d) Discuss or comment on the following:
- (i) Sources of carbon in carbido-containing clusters;
- (ii) Encapsulated carbon atoms in larger metal clusters such as Ru₆C(CO)₁₇ are relatively unreactive and it is the smaller clusters such as Fe₄C(CO)₁₃ that have shown the greatest chemical activity. [8]
- (e) Consider the following species:
- (i) Mn(CO)₅; (ii) $[\text{Fe}(\text{CO})_3]^-$; (iii) Fe₅C(CO)₁₅.
- With which of these species are $[\text{Fe}_5\text{C}(\text{CO})_{14}]^{2-}$, Co(CO)₃ and Re(CO)₅ isoelectronic so far as valence electrons are concerned? [3]

QUESTION THREE

- (a) (i) What is the "lanthanide contraction"?
- (ii) What are the consequences of the "lanthanide contraction" on the chemistry of later elements? [5]
- (b) (i) Mention the methods used to separate the lanthanide elements from each other;
- (ii) Explain in detail the most important and widely used method. [6]
- (c) Contrast the electronic spectra of the lanthanide and transition metal ions. Why do the lanthanide ions give rise to very sharp bands unlike the broad bands in the spectra of the 3d elements? [5]
- (d) Which Ln³⁺ ion would you expect to show the same colour as Eu³⁺? Justify your answer. [4]
- (e) (i) Use Hund's rules to derive the ground state term of Pr³⁺ ion;
- (ii) Hence, determine the magnetic moment, μ. [5]

QUESTION FOUR

- (a) Most industrial processes using a catalyst are heterogeneous. What factors could have led to the decision to use a homogeneous catalyst for alkene hydroformylation? [6]
- (b) (i) State the two common methods for the preparation of metal carbonyls and illustrate your answer with chemical equations. [4]
(ii) Explain the observation that the ligand cyclohepta-1,3,5-triene is hexahapto when bonded to the $\text{Cr}(\text{CO})_3$ fragment, but only tetrahapto when bonded to the $\text{Fe}(\text{CO})_3$ fragment. [3]
- (c) Formulate neutral, 18-electron complexes of chromium (Cr) which contain only
(i) cyclopentadienyl and nitrosyl ligands;
(ii) cyclopentadienyl, carbonyl, and nitrosyl ligands. [4]
- (d) (i) Give an example of a pseudohalogen;
(ii) Give two properties to show why the example in question (4)(d)(i) above is referred to as a pseudohalogen. [3]
- (e) (i) Name one cationic, one neutral, and one anionic interhalogen compound.
(ii) In those interhalogen compounds consisting of three or more atoms, state the rule that predicts which atom will be the central atom. [5]

QUESTION FIVE

- (a) **M** is a first transition series element. It forms a carbonyl **F** of empirical formula $M(CO)_5$ which reacts with sodium amalgam in tetrahydrofuran to give a solution **G**. Treatment of **G** with 3-chloro-1-propene gives a compound **H** of molecular formula $C_8H_5O_5M$. The infrared spectrum of **H** shows carbonyl stretching bands between 2110 and 2004 cm^{-1} . On heating **H** to 100 °C one molecule of carbon monoxide is eliminated to give **I**, $C_7H_5O_4M$ [$\nu_{(CO)}$ between 2110 and 1950 cm^{-1}].
- Identify the metal **M**;
 - Propose and draw structures for the compounds **F**, **H** and **I**;
 - Give the species present in solution **G**;
 - Discuss the bonding of the organic ligand to **M** in compound **I**. [7]
- (b) Explain, with necessary diagrams the bonding in ethylene, C_2H_4 , to transition metal atoms with emphasis on the σ -donor and π^* -acceptor functions of the ligand. [5]
- (c) Account for the observation that iodine, I_2 , is almost insoluble in water but readily soluble in an aqueous solution of KI. [2]
- (d) Predict the structures of the following compounds:
- IF_7
 - ICl_2^-
 - ICl_2^+ [9]
- (e) Predict the product(s) of the following reactions:
- $Cl_2 + ClF_3 \rightarrow$
 - $BrF_5 + F_2 \rightarrow$ [2]

QUESTION SIX

- (a) Use the Arrhenius, Bronsted-Lowry, Lewis, and Solvent-System concepts with relevant equations to explain why NH_3 is a base in aqueous solution. [8]
- (b) Describe the three classes of aprotic solvents, mentioning examples of each. [6]
- (c) Addition of PPh_3 to a solution of Wilkinson's catalyst, $(PPh_3)_3RhCl$, reduces the turnover frequency for the hydrogenation of propylene. Give a plausible explanation for this observation. [3]
- (d)
 - Write balanced reaction equations in each of the following processes:
 - The Monsanto Acetic Acid process;
 - The Wacker process.
 - Choose one of the processes in question (6)(d)(i) above and outline the main steps in the possible mechanism. [8]