

**UNIVERSITY OF SWAZILAND**  
**SUPPLEMENTARY EXAMINATION**  
**ACADEMIC YEAR 2009/2010**

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**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.**

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**A PERIODIC TABLE AND OTHER USEFUL DATA HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.**

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## QUESTION ONE

(a) Determine the specified quantity:

(i) The metal-metal bond order consistent with the 18-electron rule for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2]_2^{2-}$ .

(ii) The identity of the first row-transition metal in  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$  (assume a single M-M bond), an 18-electron molecule.

(iii) The expected charge on  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^z$  on the basis of the 18-electron rule. [3]

(b) Explain why  $\text{V}(\text{CO})_6$  is easily reduced to the monoanion,  $[\text{V}(\text{CO})_6]^-$  [4]

(c) Identify the following reactions by type and predict the products:

(i)  $\text{Re}_2(\text{CO})_{10} + \text{Na/Hg} \rightarrow$

(ii)  $\text{Rh}(\text{PPh}_3)_3\text{Br} + \text{Cl}_2 \rightarrow$  [4]

(d) (i) Suggest a sequence of reactions for the preparation of  $\text{Fe}(\text{CO})_3(\text{diphos})$ , given iron metal, CO, diphos ( $\text{Ph}_2\text{P-CH}_2\text{-CH}_2\text{-PPh}_2$ ), and other reagents of your choice.

(ii) Propose a synthesis for  $\text{HMn}(\text{CO})_5$ , starting with  $\text{Mn}_2(\text{CO})_{10}$  as the source of Mn and other reagents of your choice. [10]

(e) Select the best choice in each of the following, and briefly justify the reason for your selection.

(i) Shortest C-O bond:  $\text{Ni}(\text{CO})_4$ ,  $[\text{Co}(\text{CO})_4]^-$ ,  $[\text{Fe}(\text{CO})_4]^{2-}$

(ii) Highest C-O stretching frequency:  $\text{Ni}(\text{CO})_3(\text{PF}_3)$ ,  $\text{Ni}(\text{CO})_3(\text{PCl}_3)$ ,  
 $\text{Ni}(\text{CO})_3(\text{PMe}_3)$  [4]

## QUESTION TWO

- (a) The reaction of chloroform with  $\text{Co}_2(\text{CO})_8$  yields a compound of formula  $\text{Co}_3(\text{CH})(\text{CO})_9$ . NMR and IR data indicate the presence of only terminal CO ligands and the presence of a CH group. Propose a structure consistent with the spectra and the correlation of cluster valence electron (CVE) count with structure. [5]
- (b) Give organic fragments isolobal with each of the following:  
(i)  $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}$                       (ii)  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$   
(iii)  $[\text{Fe}(\text{CO})_2(\text{PPh}_3)]^-$  [3]
- (c) Use Wade's rules to predict the structures of the following:  
(i)  $\text{B}_5\text{H}_8^-$                                       (ii)  $\text{Os}_5(\text{CO})_{16}$   
(ii)  $\text{Os}_6(\text{CO})_{17}[\text{P}(\text{OMe}_3)]_3$  [6]
- (d) (i) Give a definition of a metal cluster.  
(ii) What are the two broad classes of metal carbonyl clusters?  
(iii)  $\text{M}_3(\text{CO})_{12}$  clusters ( $\text{M} = \text{Ru}$  and  $\text{Os}$ ) are unreactive. Give three ways by which they can be converted into more reactive derivatives. [9]
- (e) What are the formulas of the metal carbonyls that are isoelectronic with  
(i)  $\text{Co}(\text{NO})_3$   
(ii)  $\text{Fe}(\text{CO})_2(\text{NO})_2$ ? [2]

## QUESTION THREE

- (a) Explain with necessary diagrams the bonding in CO to transition metal atoms with emphasis on the  $\sigma$ -donor and  $\pi^*$ -acceptor functions of the ligand. [4]
- (b) The complex  $[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$  can be used in the catalytic synthesis of n-pentanal from an alkene having one less carbon atom.  
(i) Outline the main steps in the mechanism of this process indicating the reaction type of each step (such as oxidative addition) and identifying the catalytic species. [10]  
(ii) Increasing the concentration of phosphine in the phosphine-rhodium cycle slows the reaction rate. Explain. [5]
- (c) Using the most appropriate acid-base theory, identify the acids and bases in the following reactions:  
(i)  $\text{SiO}_2 + \text{Na}_2\text{O} = \text{Na}_2\text{SiO}_3$   
(ii)  $\text{B}(\text{OR})_3 + \text{NaH} = \text{Na}[\text{HB}(\text{OR})_3]$   
(iii)  $\text{Cl}_3\text{PO} + \text{Cl}^- = \text{Cl}_4\text{PO}^-$  [6]

#### QUESTION FOUR

- (a) (i) Why is it difficult to separate lanthanide ions?  
(ii) A mixture of lanthanide metal ions was prepared containing  $\text{Ce}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Yb}^{3+}$ . To separate the ions, a portion of the solution of the ions was poured through a sulphonated polystyrene ion-exchange resin. The column was then eluted with a dilute solution of  $\text{H}_4\text{EDTA}$  adjusted to pH 8 with ammonia.  
(1) Which ion comes out first? Explain.  
(2) Suggest another buffer solution that could be used to elute the ions from the column. [9]
- (b) An empty, a half-filled and a completely filled  $4f$  electronic level is often said to confer stability on the oxidation state of a lanthanide ion. Cite examples which bear out this statement. [3]
- (c) (i) Use Hund's rules to derive the ground state term of  $\text{Nd}^{3+}$ .  
(ii) Hence determine the magnetic moment,  $\mu$ . [6]
- (d) What are the main sources of  
(i) Thorium, (Th)  
(ii) Uranium, (U) [4]
- (e) Work out the number of unpaired electrons in the ions  
(i)  $\text{Gd}^{3+}$   
(ii)  $\text{Tm}^{3+}$   
(iii)  $\text{Lu}^{2+}$  [3]

### QUESTION FIVE

- (a) Describe the main types of interhalogen compounds giving examples of each. [6]
- (b) Predict the products of the following reactions of interhalogens:  
(i)  $\text{ClF} + \text{S} \rightarrow$   
(ii)  $\text{ClF}_3 + \text{SbF}_5 \rightarrow$   
(iii)  $\text{IF}_5 + \text{CsF} \rightarrow$  [3]
- (c) Given that 1.84 g of  $\text{IF}_3$  reacts with 0.93 g of  $[(\text{CH}_3)_4\text{N}]\text{F}$  to form a product **X**:  
(i) identify **X**  
(ii) Use VSEPR model to predict the shapes of  
(1)  $\text{IF}_3$   
(2) the cation in **X**  
(3) the anion in **X** [8]
- (d) The interhalogen compound,  $\text{I}_2\text{Cl}_6$  exists as a dimer in the solid state.  
(i) Write a balanced equation for the preparation of this compound. [2]  
(ii)  $\text{I}_2\text{Cl}_6$  undergoes dissociation on warming to room temperature. Write the reaction for the dissociation process. [3]
- (e) Ligand substitution reactions on metal clusters are often found to occur by associative mechanisms, and it is postulated that these occur by initial breaking of an M-M bond, thereby providing an open coordination site for the incoming ligand. If the proposed mechanism is applicable, which would you expect to undergo the fastest exchange with added  $^{13}\text{C}$ O?  $\text{Co}_4(\text{CO})_{12}$  or  $\text{Ir}_4(\text{CO})_{12}$ ? Suggest an explanation. [3]

## QUESTION SIX

- (a) Indicate with sketches the structures of the following:
- (i)  $\text{LiCH}_3$
  - (ii)  $\text{Hg}(\text{CH}_3)_2$
  - (iii)  $\text{Al}(\text{CH}_3)_3$  [6]
- (b) (i) How is an alkylidene triphenylphosphorane (Wittig reagent) made?  
(ii) What is it used for? [4]
- (c) Select the best answer and give the basis for your selection.
- (i) Strongest acid:  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  or  $\text{H}_2\text{Te}$
  - (ii) Stronger base:  $\text{NF}_3$  or  $\text{NH}_3$  [4]
- (d) Use the hard and soft acid base (HSAB) theory to predict which of the following pairs of adducts should be the more stable:
- (i)  $[\text{Fe}(\text{NMe}_3)_6]^{3+}$  or  $[\text{Fe}(\text{SbMe}_3)_6]^{3+}$
  - (ii)  $\text{BeI}_2$  or  $\text{BeF}_2$  [4]
- (e) (i) Draw the Lewis diagrams for all the species involved in the reaction  
$$2\text{HSO}_3\text{F} = \text{H}_2\text{SO}_3\text{F}^+ + \text{SO}_3\text{F}^-$$
  
(ii) Discuss this equilibrium
- (1) in terms of the solvent-system definition of acids and bases.
  - (2) in terms of the Lewis definition of acids and bases. [7]

# PERIODIC TABLE OF ELEMENTS

## GROUPS

PERIODS	1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18	
	IA	IIA	IIIB	IVB	VB	VIB	VIIA	VIIIB	VIIIB	VIIIB	VIIIB	VIIIB	VIIIB	VIIIB	VIIIB	VIIIB	VIIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IIIA	IIIA	IIIA	IIIA	IIIA	IIIA	IIIA	IIIA	IIIA	IIIA	IIIA	VIIIA	
1	H 1																																		He 2	
2	Li 3	Be 4																																	Ne 10	
3	Na 11	Mg 12																																	Ar 18	
<b>TRANSITION ELEMENTS</b>																																				
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36																		
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54																		
6	Cs 55	Ba 56	*La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86																		
7	Fr 87	Ra 88	**Ac 89	Rf 104	Ha 105	Unh 106	Uns 107	Uno 108	Une 109	Uun 110																										

Atomic mass  
Symbol  
Atomic No.

<b>*Lanthanide Series</b>											
140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93
Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69
<b>**Actinide Series</b>											
232.04	231.04	238.03	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)
Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101
174.97											
Lu 71											
(260)											
Lr 103											

( ) indicates the mass number of the isotope with the longest half-life.

## General data and fundamental constants

Quantity	Symbol	Value
Speed of light	$c$	$2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$
Elementary charge	$e$	$1.602\,177 \times 10^{-19} \text{ C}$
Faraday constant	$F = N_A e$	$9.6485 \times 10^4 \text{ C mol}^{-1}$
Boltzmann constant	$k$	$1.380\,66 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	$R = N_A k$	$8.314\,51 \text{ J K}^{-1} \text{ mol}^{-1}$ $8.205\,78 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ $6.2364 \times 10 \text{ L Torr K}^{-1} \text{ mol}^{-1}$
Planck constant	$h$	$6.626\,08 \times 10^{-34} \text{ J s}$
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34} \text{ J s}$
Avogadro constant	$N_A$	$6.022\,14 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit	$u$	$1.660\,54 \times 10^{-27} \text{ Kg}$
Mass		
electron	$m_e$	$9.109\,39 \times 10^{-31} \text{ Kg}$
proton	$m_p$	$1.672\,62 \times 10^{-27} \text{ Kg}$
neutron	$m_n$	$1.674\,93 \times 10^{-27} \text{ Kg}$
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$ $4\pi\epsilon_0$	$8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ $1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Vacuum permeability	$\mu_0$	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$ $4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ C}^{-2} \text{ m}^3$
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24} \text{ J T}^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27} \text{ J T}^{-1}$
g value	$g_e$	2.002 32
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar/m_e e^2$	$5.291\,77 \times 10^{-11} \text{ m}$
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c \epsilon_0^2$	$1.097\,37 \times 10^7 \text{ m}^{-1}$
Standard acceleration of free fall	$g$	$9.806\,65 \text{ m s}^{-2}$
Gravitational constant	$G$	$6.672\,59 \times 10^{-11} \text{ N m}^2 \text{ Kg}^{-2}$

## Conversion factors

1 cal	4.184 joules (J)	1 erg	$1 \times 10^{-7} \text{ J}$
1 eV	$1.602\,2 \times 10^{-19} \text{ J}$	1 eV/molecule	$96\,485 \text{ kJ mol}^{-1}$ $23.061 \text{ kcal mol}^{-1}$

f	p	n	$\mu$	m	c	d	k	M	G	Prefixes
fermi	pico	nano	micro	milli	centi	deci	kilo	mega	giga	
$10^{-15}$	$10^{-12}$	$10^{-9}$	$10^{-6}$	$10^{-3}$	$10^{-2}$	$10^{-1}$	$10^3$	$10^6$	$10^9$	

## Spectrochemical Series

$\Gamma < \text{Br}^- < \text{S}^{2-} < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{EtOH} < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{EDTA} < (\text{NH}_3, \text{py}) < \text{en} < \text{dipy} < \text{NO}_2^- < \text{CN}^- < \text{CO}$