UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2014/2015

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.

PLEASE DO NOT OPEN THIS PAPER UNTIL AUTHORISED TO DO SO BY THE CHIEF INVIGILATOR.

QUESTION ONE

(a) What are the oxidation states of the transition metals in each of the following compounds?

(i) $Ti(NEt_2)_4$

(ii) $NiBr_3(PEt_3)_2$ [2]

(b) (i) Suggest a synthesis for:

(1) $Na[B(C_2H_5)_4]$

(2) C_2H_5MgBr

(ii) Write equations for a two-step preparation of $(\eta^5\text{–}C_5H_5)_2Ni$ from C_5H_6, Na, and $NiCl_2$. [8]

(c) Discuss the mechanism of the synthesis of alkenes from aldehydes or ketones by use of the Wittig reaction. [4]

(d) (i) Draw the structure of each of the organometallic substances found in the following reaction:

$$Mo(CO)_6 + C_7H_8 \xrightarrow{reflux} Mo(CO)_3C_7H_8 + 3CO$$

(ii) Would you expect Zeise's salt anion, $[PtCl_3C_2H_4]^-$ to add other ligands readily? Explain. [7]

(e) Explain mechanistically why transition metal alkyls that have a β–hydrogen atom are usually unstable, whereas analogous compounds in which the alkyls do not have β–hydrogen atoms generally are stable. [4]

QUESTION TWO

(a) (i) In what ways can CO be bound to a metal atom?

(ii) Why are the simplest carbonyls of the metals Mn, Tc, Re and Co, Rh, Ir groups polynuclear? [6]

(b) (i) In order to have a neutral vanadium carbonyl that satisfies the noble gas formalism, what would be the simplest formula?

(ii) Why do you think this fails to occur? [4]

(c) Explain the variation in the following rates for the oxidative addition reaction between MeI and $IrX(CO)L_2$ as X and L are changed:

(i) $X = F > Cl > Br > I$

$\longrightarrow$

Rate decrease

(ii) $L = PMe_2Ph > PEt_3 > PEt_2Ph > PEtPh_2 > PPh_3$

$\longrightarrow$

Rate decrease [6]

(d) Explain the following:

(i) variation in IR C–O stretching frequencies in *fac*-$(R_3P)_3Mo(CO)_3$ complexes:

R	ν_{C-O} (cm^{-1})
F	2074, 2026
Cl	2041, 1989
Ph	1949, 1835

(ii) $Co(\eta^5\text{-}C_5H_5)_2$ reacts with alkyl halides (RX) to give $[Co(\eta^5\text{-}C_5H_5)_2]^+$ and $[Co(\eta^4\text{-}C_5H_5R)(\eta^5\text{-}C_5H_5)]$.

(iii) $Mo(py)_2(CO)_4$ has two forms, one having a single CO stretching band in the IR spectrum, the other four. [9]

QUESTION THREE

(a) (i) Describe with the aid of an example what isolobal analogy means.

(ii) What are the formulas of the metal carbonyls that are isoelectronic with

(1) $Cr(NO)_4$? (2) $Mn(CO)(NO)_3$?

(3) $Mn(CO)_4NO$? [6]

(b) (i) (1) What is an insertion reaction?

(2) Give two real examples.

(ii) What is the difference between a π-acid ligand like RNC (CO analog) and a ligand like C_2H_4 (ethylene) that forms π complexes? [6]

(c) On the basis of cluster valence electron (CVE) count, predict and sketch the structures of the species given below:

(i) $Fe_5C(CO)_{15}$ (ii) $Ni_5Os(CO)_{14}$ [4]

(d) Using the Polyhedral Skeletal Electron Pair Theory (PSEPT) predict the structures of the following clusters:

(i) $[Rh_6(CO)_{16}]$ (ii) $[HRu_5C(CO)_{14}]^-$

(iii) $[Re_8C(CO)_{20}(PF_3)_4]^{2-}$ [9]

QUESTION FOUR

(a) (i) Work out the number of unpaired electrons in the ions

(1) Pr^{3+} (2) Pm^{3+} (3) Sm^{2+}

(ii) Determine the ground-state term symbol for a Dy^{3+} ion and calculate the expected magnetic moment (μ) value. [6]

(b) (i) What is characteristic about the coordination numbers of lanthanide ions? Give examples.

(ii) What are the characteristic precipitation reactions of lanthanide +2, +3, and +4 ions?

(iii) Why is it that lanthanide ions form the strongest bonds with the most electronegative ligands? [9]

(c) (i) Which +3 ion has its 5*f* shell half full?

(ii) What oxidation state does the preceding element show?

(iii) What oxidation state does the succeeding element show? [3]

(d) Do you think that carbonyls of the lanthanides are likely to be stable? Justify your answer. [3]

(e) Compare and contrast the chemistry of the dioxo ions of U, Np, Pu, and Am. [4]

QUESTION FIVE

(a) (i) Describe the bonding in
(1) $[I_3]^+$. (2) $[I_3]^-$.
(ii) Iodine has a very low solubility in water, but dissolves readily in KI (aq.). Why? [6]

(b) (i) Write a balanced equation showing the overall (net) reaction in each of the following processes:
(1) hydroformylation (2) the Ziegler–Natta process
(ii) Outline the mechanism of the Wacker process. [9]

(c) The complex $[\eta^5\text{-}C_5H_5Re(CO)_2NO]^+$ can be reduced using $NaBH_4$ in THF–water mixtures giving first a formyl complex, $\eta^5\text{-}C_5H_5Re(CO)(NO)\text{–}C(=O)H$, second a hydroxymethyl complex, $\eta^5\text{-}C_5H_5Re(CO)(NO)\text{–}CH_2OH$, and third a methyl complex, $\eta^5\text{-}C_5H_5Re(CO)(NO)\text{–}CH_3$. Determine whether or not the four compounds obey the 18-electron rule. [4]

(d) $Ni[P(OEt)_3]_4$ is used to catalyse the process

$$CH_2{=}CH\text{–}CH{=}CH_2 + HCN \rightarrow NC(CH_2)_4CN$$

Suggest a sensible sequence of steps. [6]

QUESTION SIX

(a) Name <u>five</u> properties that determine the utility of a solvent. [5]

(b) Give the autodissociation reactions of the following compounds:

(i) H_2SO_4 (ii) NH_3 (iii) IF_5 (iv) Cl_3PO [4]

(c) (i) State the Bronsted-Lowry definition of acids and bases.
(ii) State the Lewis definition of acids and bases and write <u>three</u> equations that illustrate it, including <u>one</u> that involves a protonic acid. [6]

(d) Consider acetic acid, CH_3COOH, as a solvent. Its dielectric constant is about 10.
(i) What is its mode of self-ionization likely to be?
(ii) Name one substance that will be an acid in acetic acid.
(iii) Name one substance that will be a base in acetic acid.
(iv) Will acetic acid be a better or poorer solvent than H_2O for ionic compounds? (Dielectric constant of $H_2O = 82$). [4]

(e) (i) Explain why dimethyl sulphoxide, DMSO, is a very good solvent for polar and ionic materials.
(ii) Why do you think phosphines (R_3P) and phosphine oxides (R_3PO) differ considerably in their base properties? [6]

PERIODIC TABLE OF ELEMENTS

PERIODS	GROUPS 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1.008 **H** 1																	4.003 **He** 2
2	6.941 **Li** 3	9.012 **Be** 4											10.811 **B** 5	12.011 **C** 6	14.007 **N** 7	15.999 **O** 8	18.998 **F** 9	20.180 **Ne** 10
3	22.990 **Na** 11	24.305 **Mg** 12											26.982 **Al** 13	28.086 **Si** 14	30.974 **P** 15	32.06 **S** 16	35.453 **Cl** 17	39.948 **Ar** 18
4	39.098 **K** 19	40.078 **Ca** 20	44.956 **Sc** 21	47.88 **Ti** 22	50.942 **V** 23	51.996 **Cr** 24	54.938 **Mn** 25	55.847 **Fe** 26	58.933 **Co** 27	58.69 **Ni** 28	63.546 **Cu** 29	65.39 **Zn** 30	69.723 **Ga** 31	72.61 **Ge** 32	74.922 **As** 33	78.96 **Se** 34	79.904 **Br** 35	83.80 **Kr** 36
5	85.468 **Rb** 37	87.62 **Sr** 38	88.906 **Y** 39	91.224 **Zr** 40	92.906 **Nb** 41	95.94 **Mo** 42	98.907 **Tc** 43	101.07 **Ru** 44	102.91 **Rh** 45	106.42 **Pd** 46	107.87 **Ag** 47	112.41 **Cd** 48	114.82 **In** 49	118.71 **Sn** 50	121.75 **Sb** 51	127.60 **Te** 52	126.90 **I** 53	131.29 **Xe** 54
6	132.91 **Cs** 55	137.33 **Ba** 56	138.91 ***La** 57	178.49 **Hf** 72	180.95 **Ta** 73	183.85 **W** 74	186.21 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.97 **Au** 79	200.59 **Hg** 80	204.38 **Tl** 81	207.2 **Pb** 82	208.98 **Bi** 83	(209) **Po** 84	(210) **At** 85	(222) **Rn** 86
7	223 **Fr** 87	226.03 **Ra** 88	(227) ****Ac** 89	(261) **Rf** 104	(262) **Ha** 105	(263) **Unh** 106	(262) **Uns** 107	(265) **Uno** 108	(266) **Une** 109	(267) **Uun** 110								

Atomic mass → 10.811
Symbol → **B**
Atomic No. → 5

TRANSITION ELEMENTS

***Lanthanide Series**	140.12 **Ce** 58	140.91 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.96 **Eu** 63	157.25 **Gd** 64	158.93 **Tb** 65	162.50 **Dy** 66	164.93 **Ho** 67	167.26 **Er** 68	168.93 **Tm** 69	173.04 **Yb** 70	174.97 **Lu** 71
****Actinide Series**	232.04 **Th** 90	231.04 **Pa** 91	238.03 **U** 92	237.05 **Np** 93	(244) **Pu** 94	(243) **Am** 95	(247) **Cm** 96	(247) **Bk** 97	(251) **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(260) **Lr** 103

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