UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION

ACADEMIC YEAR 2013/2014

TITLE OF PAPER:	**ADVANCED INORGANIC CHEMISTRY**
COURSE NUMBER:	**C401**
TIME ALLOWED:	**THREE (3) HOURS**
INSTRUCTIONS:	**THERE ARE SIX (6) QUESTIONS. ANSWER <u>ANY FOUR (4)</u> QUESTIONS. EACH QUESTION IS WORTH 25 MARKS.**

A PERIODIC TABLE HAS BEEN PROVIDED WITH THIS EXAMINATION PAPER.

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QUESTION ONE

(a) Write the formulae of the following compounds:
  (i) Dicarbonyl-η^5-cyclopentadienyl-η^1-cyclopentadienyliron(II).
  (ii) Dichlorobis(η^5-cyclopentadienyl)titanium(IV). [4]

(b) (i) Describe the 18-electron rule and explain its basis.
  (ii) Define a metal cluster.
  (iii) Give the electron count for each of the following species, and determine which of them obey the 18-electron rule:
    (1) Heptahaptocycloheptatrienyltricarbonylmolybdenum(I). [8]
    (2) $(CO)Os(\equiv CPh)(PPh_3)_2Cl$

(c) Explain why $V(CO)_6$ is easily reduced to the monoanion. [4]

(d) (i) Considering the bonding in metal carbonyls, what factors would affect the C–O stretching vibrations?
  (ii) A carbonyl complex has linear OC-M-CO group. How will the CO stretching frequency change (increase, decrease or remain the same) under the following conditions? Justify your answers.
    (1) One CO is replaced by triethylamine, $(CH_3CH_2)_3N$:
    (2) The complex acquires a positive charge
    (3) The complex acquires a negative charge [9]

QUESTION TWO

(a) Explain, with necessary orbital diagrams, how carbon monoxide, CO, which has negligible donor properties toward simple acceptors such as BF_3, can form strong bonds to transition metal atoms. [8]

(b) Based on isolobal analogies, choose the organometallic fragments that might replace

(i)	CH_2^+	$Fe(CO)_4$, $Mn(CO)_5$, or $Re(CO)_4$
(ii)	CH^-	$Ni(CO)_3$, $Co(CO)_3$, or $Mn(CO)_4$
(iii)	CH_3	$CpCo(CO)$, $Mn(CO)_5$, or $Cr(CO)_6$ [3]

(c) (i) Classify each of the following as closo, nido or arachno:
    (1) $Rh_6(CO)_{16}$ (2) $Os_5C(CO)_{15}$
  (ii) Describe the structures of the above species. [8]

(d) Predict the transition metal-containing products of the following reactions:
  (i) $Mo(CO)_6 + Ph_2P\text{-}CH_2\text{-}PPh_2 \rightarrow$
  (ii) $H_3C\text{-}Mn(CO)_5 + SO_2 \rightarrow$ (no gases are evolved)
  (iii) $Rh(CO)_3Br + H_2 \rightarrow$ [6]

QUESTION THREE

(a) Discuss briefly the two types of insertion reactions encountered in homogeneous catalysis. [6]

(b) Explain the following observations:

(i) The ligand CO can be replaced from $Ni(CO)_4$ by PF_3 or $SbCl_3$, but no reaction occurs with PF_5 or $SbCl_5$.

(ii) The ligand cyclohepta-1,3,5-triene is hexahapto when bonded to the $Cr(CO)_3$ fragment, but only tetrahapto when bonded to the $Fe(CO)_3$ fragment. [6]

(c) Outline the mechanism for the alkene hydrogenation using $RhCl(PPh_3)_3$ as the catalyst. [13]

QUESTION FOUR

(a) Give two separation methods that can produce the pure elements with little contamination from the other lanthanides. Describe one in detail. [6]

(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) Which actinide element has the most stable +2 oxidation state?

(ii) Which actinide element forms a +3 ion with 7 electrons in the 5f orbital?

(iii) Name one actinide element that forms compounds in the +7 oxidation state. [3]

(d) (i) Determine the number of unpaired electrons in Er^{3+}.

(ii) Derive the ground state-term symbol for Er^{3+}, and calculate its magnetic moment.

(iii) Write the formula of one lanthanide metal ion whose magnetic moment can be calculated by the spin-only formula. [6]

(e) (i) Which actinide isotope(s) is/are obtained in macroscopic amounts?

(ii) What are the main principles upon which the separation of Np, Pu and Am from U are made? [7]

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) $ICl + KI \rightarrow$

(ii) $ClF_3 + SbF_5 \rightarrow$

(iii) $IF_5 + CsF \rightarrow$ [3]

(c) Based on the analogy between halogens and pseudohalogens, write the balanced equation for the probable reaction of

(i) cyanogens, $(CN)_2$ with aqueous hydroxide.

(ii) cyanide ion, (CN^-) with lead ion, (Pb^{2+}). [2]

(d) Draw the structure and write an equation for the preparation for each of the following compounds:

(i) I_3^+ (ii) BrF_5 [10]

(e) The interhalogen, I_2Cl_6 exists as a dimer in the solid state.

(i) Write a balanced equation for the preparation of this compound.

(ii) I_2Cl_6 undergoes dissociation on warming to room temperature. Write the reaction for the dissociation process. [4]

QUESTION SIX

(a) Name two common impurities in solvents and indicate how they can be removed. [4]

(b) (i) Use the HSAB theory to predict which of the following pairs of adducts should be the more stable:

(1) $[Fe(NMe_3)_6]^{3+}$ or $[Fe(SbMe_3)_6]^{3+}$

(2) BeI_2 or BeF_2

(ii) Select the best answer and give the basis for your selection.

(1) Strongest acid: H_2O, H_2S, H_2Se or H_2Te

(2) Stronger base: NF_3 or NH_3 [8]

(c) Consider each of the following solvents:

(I) Ammonia, NH_3 (II) Acetic acid, CH_3COOH

(III) Sulphuric acid, H_2SO_4

(i) Give equations for autoionisation of the pure solvents.

(ii) Give appropriate equations to show what will happen if CH_3COOH is dissolved in

(1) NH_3

(2) H_2SO_4 [5]

(d) (i) State the Bronsted-Lowry definition of acids and bases.

(ii) State the Lewis definition of acids and bases and write two equations that illustrate it, including one that involves a protonic acid. [4]

(e) Predict whether the equilibrium constants for the following reactions should be greater than 1 (reaction lies to the right) or less than 1 (reaction lies to the left):

(i) $CdI_2 + CaF_2 \leftrightarrows CdF_2 + CaI_2$

(ii) $[CuI_4]^{2-} + [CuCl_4]^{3-} \leftrightarrows [CuCl_4]^{2-} + [CuI_4]^{3-}$ [4]

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	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 **H** 1																	4.003 **He** 2
2	6.941 **Li** 3	9.012 **Be** 4										Atomic mass → **Symbol** → Atomic No. →	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				TRANSITION ELEMENTS							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								

***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.