UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2006

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) Determine whether or not the following compounds obey the 18-electron rule:
(i) $Mn(CO)_4NO$ (ii) $Co(H)(N_2)(PPh_3)_2$ [2]

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

(c) Briefly describe three methods of generating metal-carbon bonds. Illustrate with appropriate examples. [6]

(d) Write equations for a two step preparation of $(\eta^5\text{-}C_5H_5)_2Ni$ from C_5H_6, Na and $NiCl_2$. [4]

(e) For each of the following sets, explain the trends in the IR-active stretching frequencies (in cm^{-1}):

(i)	$[Mo(CO)_3(PF_3)_3]$	2040, 1991
	$[Mo(CO)_3(PMe_3)_3]$	1945, 1851
(ii)	$[Ni(CO)_4]$	2046
	$[Fe(CO)_4]^{2-}$	1788

[6]

(f) Identify the third row transition element which would give the most thermodynamically stable compound of the type:
(i) $[(\eta^6\text{-}C_6H_6)M(CO)_3]^+$ (ii) $(\eta^5$-cyclopentadienyl$)M(NO)$
(iii) $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$, assume a single M-M bond) [3]

QUESTION TWO

(a) Identify the following reactions by type and predict the products:
(i) $Re_2(CO)_{10} + Na/Hg \rightarrow$
(ii) $Rh(PPh_3)_3Br + Cl_2 \rightarrow$ [4]

(b) Give organic fragments isolobal with each of the following:
(i) $(\eta^5\text{-}C_5H_5)Ni$ (ii) $(\eta^6\text{-}C_6H_6)Cr(CO)_2$
(ii) $[Fe(CO)_2(PPh_3)]^-$ [3]

(c) Use Wade's rules to predict the structures of the following:
(i) B_5H_{11} (ii) $Os_6(CO)_{17}[P(OMe_3)]_3$
(iii) $[Os_{10}C(CO)_{24}]^{2-}$ [9]

(d) Consider the following species:
(i) $Cr(CO)_3$ (ii) CN^- (iii) CH_3
With which of these species are NH_2, $(\eta^5\text{-}C_5H_5)Mn$ and NO^+ isoelectronic so far as valence electrons are concerned? [3]

(e) Show how cyclohepta-1,3,5-triene is coordinated to the $Mo(CO)_3$ and $Fe(CO)_3$ fragments. [6]

QUESTION THREE

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

(b) Write balanced reaction equations showing the overall (net) reaction in each of the following processes:
(i) Hydroformylation.
(ii) The Ziegler-Natta process. [4]

(c) The complex $Rh(H)(CO)(PPh_3)_3$ 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]

QUESTION FOUR

(a) Give one example in each case of a lanthanide ion that is
(i) diamagnetic.
(ii) stable in oxidation state +4.
(iii) precipitated by sulphate ions. [6]

(b) A mixture of the lanthanide metal ions was prepared containing Ce^{3+}, Eu^{3+} and 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 H_4EDTA adjusted to pH 8 with ammonia.
(i) Which ion comes out first? Explain [4]
(ii) Suggest another buffer solution that could be used to elute the ions from the column. [1]
(iii) After the above separation procedure, one of the ions was purified, and then converted to the bromide, MBr_3. A total of 1.3209g of the bromide was dissolved in aqueous solution and an excess of silver nitrate solution was added to produce a precipitate. The mass of dried precipitate was 1.8027 g. Calculate the molar mass of the lanthanide metal M, and write its name and chemical symbol. [5]

(c) (i) Derive the ground state term symbol for Ho^{3+} ion, in the form $^{2S+1}L_J$. [4]
(ii) Calculate the theoretical magnetic moment of the ion. [2]

(d) (i) Which actinide element has the most stable +2 oxidation state?
(ii) Name one actinide element that forms compounds in the +7 oxidation state.
(iii) Which actinide element forms a +3 ion with 7 electrons in the 5f orbital? [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) $ICl + KI \rightarrow$
(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 compound, I_2Cl_6 exists as a dimmer 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) The diameter of high spin Fe(II) is larger than the 'hole' at the centre of the porphyrin ring whereas low spin Fe(II) is smaller.
(i) Draw the electronic configurations for the two spin states in an octahedral environment. [3]
(ii) Why does the high spin have a larger radius? [3]
(iii) Explain how the difference in size of the two spin states benefits the O_2 uptake by deoxyhemoglobin. [4]

(b) Why are d-block metals such as Mn, Fe, Co and Cu used in redox enzymes in preference to Zn, Ga and Ca? [3]

(c) (i) To what sort of systems does the Lux-Flood concept apply?
(ii) Give a representative equation. [3]

(d) Use the HSAB theory to predict which of the following pairs of adducts should be the more stable.
(i) $(CH_3)_3Al{:}N(CH_3)_3$ or $(CH_3)_3Al{:}Sb(CH_3)_3$
(ii)
(iii) $[Ni(H_2O)_6]^{2+}$ or $[Fe(H_2O)_6]^{3+}$ [4]

(e) Calculate the pH of 1.0 M solution of NH_4Cl in NH_3 solvent, where $pK_s = 29$, and the acidic and basic ranges. [5]

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	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.