UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2005

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 AND OTHER USEFUL DATA HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

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

QUESTION ONE

(a) Determine the specified quantity:

(i) The metal-metal bond order consistent with the 18-electron rule for $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2^{2-}$.

(ii) The identity of the first row-transition metal in $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (assume a single M-M bond), an 18-electron molecule.

(iii) The expected charge on $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^z$ on the basis of the 18-electron rule. [3]

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

(c) 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]

(d) (i) Suggest a sequence of reactions for the preparation of $Fe(CO)_3$(diphos), given iron metal, CO, diphos ($Ph_2P\text{-}CH_2\text{-}CH_2\text{-}PPh_2$), and other reagents of your choice. [5]

(ii) Propose a synthesis for $HMn(CO)_5$, starting with $Mn_2(CO)_{10}$ as the source of Mn and other reagents of your choice. [5]

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

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

(ii) Highest C-O stretching frequency: $Ni(CO)_3(PF_3)$, $Ni(CO)_3(PCl_3)$, $Ni(CO)_3(PMe_3)$ [2]

QUESTION TWO

(a) The reaction of chloroform with $Co_2(CO)_8$ yields a compound of formula $Co_3(CH)(CO)_9$. 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. [4]

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

(c) Use Wade's rules to predict the structures of the following:
(i) $B_5H_8^-$
(ii) $Os_5(CO)_{16}$
(iii) $Os_6(CO)_{17}[P(OMe_3)]_3$ [6]

(d) (i) Give a definition of a metal cluster. [1]
(ii) What are the two broad classes of metal carbonyl clusters? [2]
(iii) $M_3(CO)_{12}$ clusters (M = Ru and Os) are unreactive. Give *three* ways by which they can be converted into more reactive derivatives. [6]

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

QUESTION THREE

(a) Explain with necessary diagrams the bonding in CO to transitional metal atoms with emphasis on the σ-donor and π*-acceptor functions of the ligand. [10]

(b) 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) (i) Why is it difficult to separate lanthanide ions? [4]

(ii) A mixture of 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 polysterene ion-exchange resin. The column was then eluted with a dilute solution of H_4EDTA adjusted to pH 8 with ammonia.

(1) Which ion comes out first? Explain. [4]

(2) Suggest another buffer solution that could be used to elute the ions from the column. [1]

(b) An empty, a half-filled and a completely filled 4*f* 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 Nd^{3+}. [4]

(ii) Hence determine the magnetic moment, μ. [5]

(d) What are the main sources of

(i) Thorium, (Th) [2]

(ii) Uranium, (U) [2]

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) $ClF + S \rightarrow$

(ii) $ClF_3 + SbF_5 \rightarrow$

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

(c) Draw the <u>structure</u> and write an equation for its <u>preparation</u> for each of the following compounds:

(i) I_3^+

(ii) BrF_5 [8]

(d) The interhalogen compound, 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. [5]

(e) Give one example of a pseudohalogen and mention <u>two</u> relevant properties to show why it is a pseudohalogen. [3]

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PERIODIC TABLE OF ELEMENTS

PERIODS	GROUPS 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
1	1.008 **H** 1																
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
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
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
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
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
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.