UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2007

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) Give examples of each of the following reaction types:
   (i) a reaction of a metal with an organic halide
   (ii) transmetallation
   (iii) metathesis. [3]

(b) Show with drawings the expected structures of the following cyclooctatetraene (cot) complexes:
   (i) (cot)$Cr(CO)_3$.
   (ii) (cot)$Fe(CO)_3$.
   (iii) (cot)$PtCl_2$. [3]

(c) Predict the products of the following reactions:
   (i) $Os(\eta^5\text{-}C_5H_5)_2 + CH_3C(O)Cl \longrightarrow$
   (ii) $LiBu + Fe(\eta^5\text{-}C_5H_5)_2 \longrightarrow$
   (iii) $(OC)_5Mn\text{-}Mn(CO)_5 + Br_2 \longrightarrow$ [3]

(d) Suggest reasonable syntheses for
   (i) $Cr(\eta^6\text{-}C_6H_6)(CO)_3$ starting with $CrCl_3$, CO, Al, and C_6H_6.
   (ii) $H_3C\text{-}Re(CO)_5$ using Re_2O_7, CO, CH_3I and Na as the primary starting materials. [10]

(e) Discuss each of the following observations:
   (i) The symmetric CO stretching frequencies in $[V(CO)_6]^-$, $[Cr(CO)_6]$ and $[Mn(CO)_6]^+$ are 1858, 2000 and 2095 cm^{-1} respectively.
   (ii) When CO becomes coordinated to BH_3 its stretching frequency increases, but when CO becomes coordinated to $Ni(CO)_3$ its stretching frequency decreases. [6]

QUESTION TWO

(a) Using Si and a chloromethane as the primary starting materials, give equations for the synthesis of hexamethyldisiloxane. [6]

(b) Based on isolobal analogies, choose the group that might replace the group underlined in

(i) $Co_3(CO)_9\underline{CH}$ OCH_3, $N(CH_3)_2$, or $SiCH_3$

(ii) $(OC)_5Mn\underline{Mn(CO)_5}$ I, CH_2, or CCH_3 [4]

(c) Use Wade's rules to predict the structures of the following:

(i) $[Fe_4C(CO)_{12}]^{2-}$

(ii) $Os_7(CO)_{21}$ [4]

(d) Discuss/comment on the following:

(i) Sources of carbon in carbido-containing clusters.

(ii) Encapsulated carbon atoms in larger metal clusters such as $Ru_6C(CO)_{17}$ are relatively unreactive and it is the smaller clusters such as $Fe_4C(CO)_{13}$ that have shown the greatest chemical activity. [8]

(d) Consider the following species:

(i) $Mn(CO)_5$

(ii) $[Fe(CO)_3]^-$

(iii) $Fe_5C(CO)_{15}$.

With which of these species are $[Fe_5C(CO)_{14}]^{2-}$, $Co(CO)_3$ and $Re(CO)_5$ isoelectronic so far as valence electrons are concerned? [3]

QUESTION THREE

(a) What is the "lanthanide contraction"? What are its consequences on the chemistry of later elements? [5]

(b) Mention the methods used to separate the lanthanide elements from each other. Explain in detail the most important and widely used method. [6]

(c) Contrast the electronic spectra of the lanthanide and transition metal ions. Why do the lanthanide ion give rise to very sharp bands unlike the broad bands in the spectra of the 3d elements? [5]

(d) What is the structure of the redox center of HiPIP and of the 4-Fe Ferredoxins? [4]

(e) (i) Use Hund's rules to derive the ground state term of Pr^{3+} ion.

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

QUESTION FOUR

(a) Do the equilibrium positions of the following reactions lie to the left or the right?

(i) $Hb + Hb(O_2)_4 \leftrightarrows 2Hb(O_2)_2$

(ii) $Hb(O_2)_4 + 4Mb \leftrightarrows Hb + 4Mb(O_2)$

Use figure 1 below to explain your reasoning.

(iii) Does your answer in (ii) above depend on the partial pressure of O_2? [6]

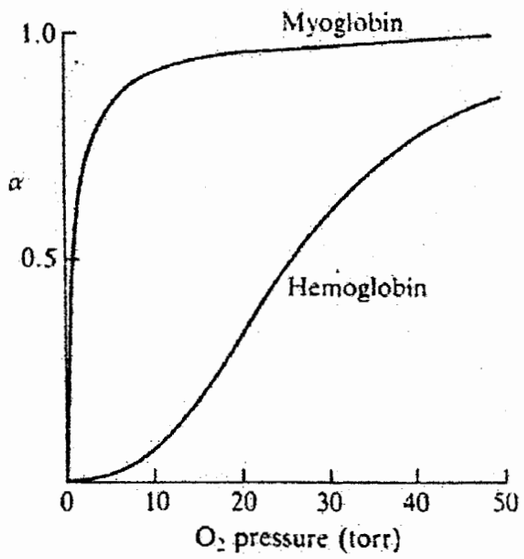

Figure 1: The oxygen saturation curves for Myoglobin (Mb) and Hemoglobin (Hb) showing the fractional oxygen saturation α as a function of the oxygen partial pressure at pH 7.2

(b) What role does zinc ion play in the action of carboxypeptidase? [2]

(c) (i) What is a cobaloxime and of what interest are cobaloximes? [2]

(ii) List the ways in which the cobaloximes resemble cobalamin. [7]

(d) Give an example of a pseudohalogen and <u>two</u> properties to show why it is referred to as a pseudohalogen? [3]

(e) (i) Name one cationic, one neutral, and one anionic interhalogen compound.

(ii) In those interhalogen compounds consisting of three or more atoms, state the rule that predicts which atom will be the central atom. [5]

QUESTION FIVE

(a) **M** is a First Transition Series element. It forms a carbonyl **F** of empirical formula $M(CO)_5$ which reacts with sodium amalgam in tetrahydrofuran to give a solution **G**. Treatment of **G** with 3-chloro-1-propene gives a compound **H** of molecular formula $C_8H_5O_5M$. The infrared spectrum of **H** shows carbonyl stretching bands between 2110 and 2004 cm^{-1}. On heating **H** to 100 °C one mole of carbon monoxide is eliminated to give **I**, $C_7H_5O_4M$ [$\nu_{(CO)}$ between 2110 and 1950 cm^{-1}].

(i) Identify the metal **M**. [1]

(ii) Propose and draw structures for the compounds **F**, **H** and **I**. [3]

(iii) Give the species present in solution **G**. [1]

(iv) Discuss the bonding of the organic ligand to **M** in compound **I**. [2]

(b) Explain, with necessary diagrams the bonding in ethylene, C_2H_4, to transition metal atoms with emphasis on the σ-donor and π-acceptor functions of the ligand [5]

(c) Account for the observation that Iodine, I_2, is almost insoluble in water but readily soluble in an aqueous solution of KI. [2]

(d) Predict the structures of the following compounds:

(i) IF_7 (ii) ICl_2^- (iii) ICl_2^+ [9]

(e) Predict the product(s) of the following reactions:

(i) $Cl_2 + ClF_3 \rightarrow$

(ii) $BrF_5 + F_2 \rightarrow$ [2]

QUESTION SIX

(a) Use the Arrhenius, Brønsted-Lowry, Lewis, and Solvent-System concepts with relevant equations to explain why NH_3 is a base in aqueous solution. [8]

(b) Describe the <u>three</u> classes of aprotic solvents, mentioning examples of each. [6]

(c) Addition of PPh_3 to a solution of Wilkinson's catalyst, $RhCl(PPh_3)_3$, reduces the turnover frequency for the hydrogenation of propylene. Give a plausible explanation for this observation. [3]

(d) (i) Write balanced reaction equations in each of the following processes:

(1) The Monsanto Acetic Acid process

(2) The Wacker process

(ii) Choose <u>one</u> of the above processes, and outline the main steps in the possible mechanism. [8]

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	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											Atomic mass → 10.811 **Symbol** → **B** Atomic No. → 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.