UNIVERSITY OF SWAZILAND

FINAL 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) 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. [3]

(ii) Give the electron count for each of the following species, and determine which of them obey the 18-electron rule.

(1) Heptahaptocycloheptatrienyltricarbonylmolybdenum(I)

(2) $(CO)Os(\equiv CPh)(PPh_3)_2Cl$ [4]

(c) Draw the structures of the following compounds:

(i) $Fe_3(CO)_{12}$ (ii) (η^5-cyclopentadienyl)$_2Cr_2(NO)_4$ [4]

(d)

(i) Considering the bonding in metal carbonyls, what factors would affect the C-O stretching vibrations? [4]

(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?

(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 [6]

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) $Os_5C(CO)_{15}$ [6]

(ii) Describe the structures of the above species. [4]

(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) [4]

QUESTION THREE

(a) By means of suitable examples, explain the following:
- (i) Oxidative addition
- (ii) Olefin metathesis
- (iii) Reductive elimination [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 $SbCl_5$. [3]
- (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. [3]

(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) From among the three elements Th, U and Np, predict which one has:
- (i) the most stable 6p orbital.
- (ii) the smallest first ionisation energy.
- (iii) the largest metallic radius. [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) are obtained in macroscopic amounts? [2]
- (ii) What are the main principles upon which the separation of Np, Pu and Am from U are made? [5]

QUESTION FIVE

(a) How are interhalogen cations prepared? Illustrate with an example. [6]

(b) Give a structure of each of the following species, and suggest a method of preparing each of them.
(i) I_3^+ (ii) IF_6^- (iii) $BrICl^-$ [6]

(c) The interhalogen compound, BrF_3, has been one of the most widely used non-aqueous solvent. Give <u>three</u> main reasons why it is such a useful solvent. [3]

(d) The interhalogen compound, IF, disproportionates on heating. Write a balanced equation for the disproportionation reaction. [1]

(e) (i) What are pseudohalogens? [1]
(ii) Discuss the most important parallels in chemistry between the halogens and pseudohalogens. [8]

QUESTION SIX

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

(b) Use the HSAB theory to predict which of the following two pairs should be more stable.
$PtCl_4^{2-}$ or PtF_4^{2-} [2]

(c) For each of the following solvents, give equations for autoionization of the pure solvents:
(i) ammonia. [1]
(ii) acetic acid. [1]
(iii) sulphuric acid. [1]

(d) Oxygen is described as a σ-base and a π-acid. Carbon monoxide, CO, is an excellent example of this type of ligand. Use these facts to propose a mechanism for CO poisoning. [3]

(e) For each of the following elements, identify one significant role in biological processes:
(i) Mn (ii) Mo (iii) Cu [3]

(f) (i) Outline the main components of cobalamin.
(ii) Distinguish between Vit. B_{12a}, Vit. B_{12r}, and Vit. B_{12s}. [10]

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	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.