UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION

ACADEMIC YEAR 2017/2018

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) (i) Determine whether or not the following compounds obey the 18-electron rule:

(1) $Mn(CO)_4NO$ (2) $Co(H)(N_2)(PPh_3)_2$ [2]

(ii) Draw the structures of the following compounds:

(1) $Fe_3(CO)_{12}$ (2) (η^5-cyclopentadienyl)$_2Cr_2(NO)_4$ [4]

(b) Briefly describe <u>three</u> methods of generating **metal-carbon** bonds. Illustrate with appropriate examples. [6]

(c) (i) Write equations for a <u>two-step</u> preparation of $(\eta^5\text{-}C_5H_5)_2Ni$ from C_5H_6, Na and $NiCl_2$.

(ii) Metal-Metal bonding in multinuclear species is not always clear-cut. *Solely on the basis of the 18-electron rule*, suggest whether $(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}PPh_2)_2Ni(\eta^5\text{-}C_5H_5)$ might be expected to contain a metal-metal bond. [4]

(d) 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]

(e) Identify the <u>third</u> 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) (η^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) $Re_2(CO)_{10} + \xrightarrow{Na/Hg}$

(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) $(\eta^6\text{-}C_6H_6)Cr(CO)_2$

(iii) $[Fe(CO)_2(PPh_3)]^-$ [3]

(c) Use Wade's rules to suggest likely structures for 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) (i) Show how cyclohepta-1,3,5-triene is coordinated to the $Mo(CO)_3$ and $Fe(CO)_3$ fragments.

(ii) 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. [6]

QUESTION THREE

(a) By means of suitable examples, explain the following:

(i) Oxidative addition (ii) Olefin metathesis

(iii) Reductive elimination [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.

(ii) Increasing the concentration of phosphine in the phosphine-rhodium cycle slows the reaction rate. Explain.. [15]

QUESTION FOUR

(a) Give three examples in each case of lanthanide ions that are
  (i) diamagnetic.
  (ii) 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.
  (ii) Suggest another buffer solution that could be used to elute the ions from the column.
  (iii) After the above separation procedure, one of the ions was purified, and then converted to the bromide, MBr_3. A total of 1.3209 g 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. [10]

(c) (i) Derive the ground state-term symbol for Ho^{3+} ion, in the form $^{2S+1}L_J$.
  (ii) Calculate the theoretical magnetic moment of the ion. [6]

(d) 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]

QUESTION FIVE

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

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

(c) The interhalogen compound, BrF_3, has been one of the most widely used non-aqueous solvent. Give three 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?
  (ii) Discuss the most important parallels in chemistry between the halogens and pseudohalogens. [9]

QUESTION SIX

(a) $H_2Os_3(CO)_{10}$ catalyses the isomerization of alkenes:

$$RCH_2CH{=}CH_2 \rightarrow E\text{-}RCH{=}CHMe + Z\text{-}RCH{=}CHMe$$

By determining the cluster valence electron count for $H_2Os_3(CO)_{10}$ deduce what makes this cluster an effective catalyst. [5]

(b) Identify the starting isotopes **A** and **B** in each of the following syntheses of transactinoid elements:

(i) **A** + ${}^{4}_{2}He \rightarrow {}^{256}_{101}Md + {}^{1}_{0}n$

(ii) **B** + ${}^{16}_{8}O \rightarrow {}^{255}_{102}No + 5({}^{1}_{0}n)$ [2]

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

(1) $(CH_3)_3Al{:}N(CH_3)_3$ or $(CH_3)_3Al{:}Sb(CH_3)_3$

(2) $[Ni(H_2O)_6]^{2+}$ or $[Fe(H_2O)_6]^{3+}$

(ii) The common ores of nickel and copper are sulphides. By contrast, aluminium is obtained from the oxide and calcium from the carbonate. Explain these observations in terms of hardness. [6]

(d) Using the most appropriate acid-base theory, identify the acids and bases in the following reactions:

(i) $SiO_2 + Na_2O \rightarrow Na_2SiO_3$

(ii) $Cl_3PO + Cl^- \rightarrow Cl_4PO^-$

(iii) $BF_3 + 2ClF \rightarrow Cl_2F^+ + BF_4^-$ [6]

(e) (i) Name <u>three</u> properties that determine the utility of a solvent.

(ii) Account for the trend in acidity:

$[Fe(OH_2)_6]^{2+} < [Fe(OH_2)_6]^{3+}$ [6]

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.