UNIVERSITY OF SWAZILAND

RE-SIT EXAMINATION

ACADEMIC YEAR 2017/2018

TITLE OF PAPER:	**COORDINATION CHEMISTRY AND CHEMISTRY OF THE TRANSITION ELEMENTS**
COURSE NUMBER:	**CHE322**
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 A TABLE OF CONSTANTS HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

NON-PROGRAMMABLE ELECTRONIC CALCULATORS MAY BE USED

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

"Marks will be awarded for method, clearly labelled diagrams, organization and presentation of thoughts in clear and concise language"

Question One

a) Give the IUPAC name for each of the following:

i) $Mo(CO)_6$
ii) $[Mn(NH_3)_6][Co(CN)_6$
iii) $[Co(urea)_6](ClO_4)_3$

[6]

b) Give the formula of each of the following:

i) Potassium tetrabromocuprate(II)
ii) Iodoaquabis(ethylenediamine)cobalt(III) nitrate
iii) Carbonatopentaamminecobalt(III) chloride

[6]

c) State the type of isomerism that may be exhibited by the following six-coordinate complexes, and draw structures of the isomers. Where appropriate, indicate whether the enathiomorph corresponds to delta, Δ, or lambda, Λ notation.

i) $[Ru(py)_3]Cl_3$
ii) $[Ru(bpy)_2Cl_2]$

[13]

Question Two

a) The first charge transfer band for $[MnO_4]^-$ occurs at 18320 cm^{-1} and that for $[MnO_4]^{-2}$ at 22940 cm^{-1}. Explain the origin of these absorption bands, and comment on the trend in relative absorption band energies on going from $[MnO_4]^-$ to $[MnO_4]^{2-}$

[6]

b) Suggest one possible and reasonable structure for each of the following complexes

i) $[TiO(acac)_2]_2$, dimeric; for each metal center, CN = 6)

ii) $[LVO]^{2+}$, where L= $(MeSCH_2CH_2)_3N$ and V= vanadium

[5]

c) Dissolution of vanadium metal in aqueous HBr solution leads to formation of a complex corresponding to formula "$VBr_3.6H_2O$". X-ray diffraction data reveal that the compound contains a cationic complex. Suggest the possible formula(s) and geometry/geometries for the complex cation(s) consistent with the x-ray diffraction data.

[6]

d) For the low-spin complex $[Co(en)(NH_3)_2(Cl_2]ClO_4$, identify the following:

- i) the coordination number of cobalt
- ii) the coordination geometry (e.g. tetrahedral, square planar, etc) for the complex ion
- iii) the oxidation number of cobalt
- iv) the electron configuration of the cobalt ion
- v) the number of unpaired electrons and whether the complex is diamagnetic or paramagnetic
- vi) the possible geometric isomers (draw the isomers)

[8]

Question Three

a) Explain the following statements

i) Atomic radius of Cr is smaller than that of Mo. On the other hand, the atomic radius of Mo is almost the same as that of W

[4]

ii) $[Ru(bpy)_3]^{2+}$ is expected to exhibit an MLCT band rather than an LMCT band

[5]

b) Using hard-soft concepts, which of the following reactions are predicted to have an equilibrium constant greater than 1? Briefly explain each of your answers.

i) $R_3PBBr_3 + R_3NBF_3 \rightleftarrows R_3PBF_3 + R_3NBBr_3$

ii) $CH_3HgI + HCl \rightleftarrows CH_3HgCl + HI$

iii) $[AgCl_2]^- + 2CN^-(aq) \rightleftarrows [Ag(CN)_2]^- + 2Cl^-$

[6]

c) The diagram below shows the splitting in an octahedral complex of the ^3F and ^3P terms arising from a d^2 configuration. Thus the ^3F term splits into $^3T_{1g}$, $^3T_{2g}$ and $^3A_{2g}$ terms. On the other hand the ^3P term is transformed into a $^3T_{1g}$ term. Due to term interaction (non-crossing rule), the $^3T_{1g}(F)$ term is lowered by x, and the $^3T_{1g}(P)$ term is raised by x. The electronic spectrum of $[V(H_2O)_6]^{3+}$, a d^2 octahedral complex, shows peaks at 17400, 25200 and 34500 cm^{-1}. Use the diagram below to assign the peaks and calculate the values of x, Δ_o and the Racah parameter B, assuming all the three peaks arise from d-d transitions.

[10]

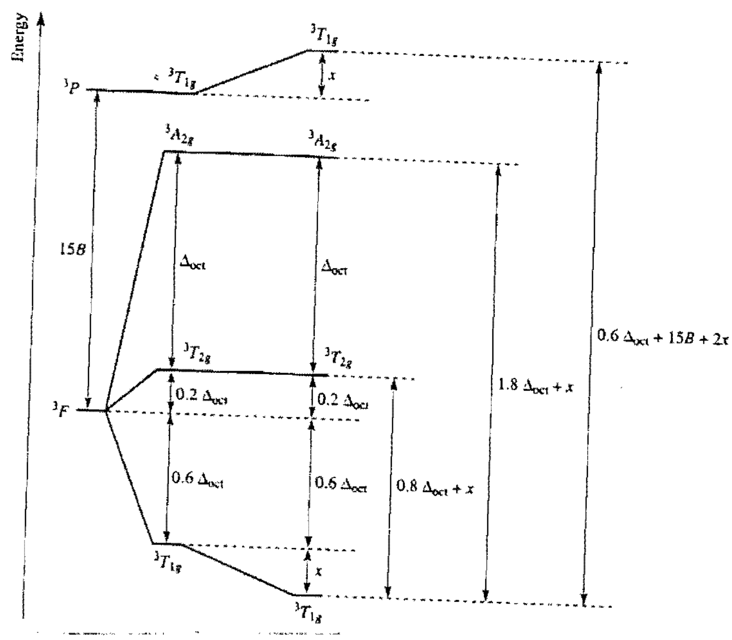

Diagram for Question 3 c)

Question Four

a) Complete and balance the following reactions:

i) $Fe + Cl_2 \xrightarrow{\Delta}$

ii) $Cr + O_2 \xrightarrow{\Delta}$

iii) $W + O_2 \xrightarrow{\Delta}$

iv) $Mn + O_2 \xrightarrow{\Delta}$

[8]

b) Draw two possible geometries for each of the following:

i) $[Mo(CN)_7]^{4-}$

ii) $[PtCl_4]^{2-}$

[6]

c) Explain each of the following:

i) $[MnCl_6]^{2-}$ is unstable whereas $[MnF_6]^{2-}$ is quite stable
ii) CrO_3 is strongly oxidizing whereas WO_3 is very weakly oxidizing

[4]

d) The anion $[CoF_6]^{3-}$ is paramagnetic, but when CN^- ions are added, the product, $[Co(CN)_6]^{3-}$, is diamagnetic. Explain this observation.

[7]

Question Five

a) Define and give one example or illustration of each of the following

i) Inner-sphere redox reaction mechanism
ii) Outer-sphere redox reaction mechanism

[8]

b) Define and give one example or illustration of each of the following

i) Kinetically inert complex
ii) Anation reaction
iii) Self-exchange electron transfer

[9]

iv) Using a sequence of reaction equations, give an outline of how you would prepare the following:

i) cis-$[PtCl_2(NH_3)_2]$
ii) cis-$[PtCl_2(NH_3)_2]$

[8]

Question Six

a) Complete and balance the following acid-base reactions:

i) $Cr_2O_3 + H^+(aq) \longrightarrow$

ii) $TiCl_4 + H_2O \longrightarrow$

iii) $V + O_2 \xrightarrow{\Delta}$

iv) $Ti + O_2 \xrightarrow{\Delta}$

[8]

b) Draw a reasonable structure of each of the following:

iii) $[TiO(DMSO)_5]Cl_2$

iv) CuCN, coordination no. =2

v) $CuSO_4.4NH_3$, cationic complex with coordination no. =4

vi) $VF_5(s)$, coordination no. =6

[8]

c) Identify two transition metal cations with each of the following electron configurations:

i) $[Ar]\ 3d^6$

ii) $[Ar]\ 3d^{10}$

iii) $[Kr]4d^5$

iv) $[Kr]4d^8$

[6]

d) Explain why Zn(II) compounds are diamagnetic irrespective of the coordination environment of the zinc(II) ion.

[3]

PERIODIC TABLE OF THE ELEMENTS

GROUPS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
PERIODS	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			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											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	28.0855 Si 14	30.9738 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.0983 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.9415 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	92.9064 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.906 Rh 45	106.42 Pd 46	107.868 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.904 I 53	131.29 Xe 54
6	132.905 Cs 55	137.33 Ba 56	138.906 *La 57	178.49 Hf 72	180.948 Ta 73	183.85 W 74	186.207 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.967 Au 79	200.59 Hg 80	204.383 Tl 81	207.2 Pb 82	208.980 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	(223) Fr 87	226.025 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109									

* Lanthanide series	140.115 Ce 58	140.908 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.925 Tb 65	162.50 Dy 66	164.930 Ho 67	167.26 Er 68	168.934 Tm 69	173.04 Yb 70	174.967 Lu 71
** Actinide series	232.038 Th 90	231.036 Pa 91	238.029 U 92	237.048 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

Numbers below the symbol of the element indicates the atomic numbers. Atomic masses, above the symbol of the element, are based on the assigned relative atomic mass of ^{12}C = exactly 12; ( ) indicates the mass number of the isotope with the longest half-life.

SOURCE: International Union of Pure and Applied Chemistry, I. Mills, ed., *Quantities, Units, and Symbols in Physical Chemistry*, Blackwell Scientific Publications, Boston, 1988, pp 86-98.

Fundamental Physical Constants (six significant figures)

Avogadro's number	N_A	$= 6.02214\times10^{23}$/mol
atomic mass unit	amu	$= 1.66054\times10^{-27}$ kg
charge of the electron (or proton)	e	$= 1.60218\times10^{-19}$ C
Faraday constant	F	$= 9.64853\times10^{4}$ C/mol
mass of the electron	m_e	$= 9.10939\times10^{-31}$ kg
mass of the neutron	m_n	$= 1.67493\times10^{-27}$ kg
mass of the proton	m_p	$= 1.67262\times10^{-27}$ kg
Planck's constant	h	$= 6.62607\times10^{-34}$ J·s
speed of light in a vacuum	c	$= 2.99792\times10^{8}$ m/s
standard acceleration of gravity	g	$= 9.80665$ m/s^2
universal gas constant	R	$= 8.31447$ J/(mol·K)
		$= 8.20578\times10^{-2}$ (atm·L)/(mol·K)

Rydberg constant = 1.097 x 10^7 m^{-1}

SI Unit Prefixes

p	n	µ	m	c	d	k	M	G
pico-	nano-	micro-	milli-	centi-	deci-	kilo-	mega-	giga-
10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

Conversions and Relationships

Length
SI unit: meter, m

1 km	= 1000 m
	= 0.62 mile (mi)
1 inch (in)	= 2.54 cm
1 m	= 1.094 yards (yd)
1 pm	$= 10^{-12}$ m = 0.01 Å

Volume
SI unit: cubic meter, m^3

1 dm^3	$= 10^{-3}$ m^3
	= 1 liter (L)
	= 1.057 quarts (qt)
1 cm^3	= 1 mL
1 m^3	= 35.3 ft^3

Pressure
SI unit: pascal, Pa

1 Pa	= 1 N/m^2
	= 1 kg/m·s^2
1 atm	$= 1.01325\times10^{5}$ Pa
	= 760 torr
1 bar	$= 1\times10^{5}$ Pa

Mass
SI unit: kilogram, kg

1 kg	$= 10^3$ g
	= 2.205 lb
1 metric ton (t)	$= 10^3$ kg

Energy
SI unit: joule, J

1 J	= 1 kg·m^2/s^2
	= 1 coulomb·volt (1 C·V)
1 cal	= 4.184 J
1 eV	$= 1.602\times10^{-19}$ J

Math relationships

	$\pi = 3.1416$
volume of sphere	$= \frac{4}{3}\pi r^3$
volume of cylinder	$= \pi r^2 h$

Temperature
SI unit: kelvin, K

0 K	= −273.15°C
mp of H_2O	= 0°C (273.15 K)
bp of H_2O	= 100°C (373.15 K)
T (K)	= T (°C) + 273.15
T (°C)	= [T (°F) − 32]$\frac{5}{9}$
T (°F)	= $\frac{9}{5}T$ (°C) + 32

CHE322/C301

The Hard and Soft [Lewis] Acids and Bases

Classification of Bases

Hard	Soft
H_2O, OH^-, F^-	R_2S, RSH, RS^-
$CH_3CO_2^-$, PO_4^{3-}, SO_4^{2-}	I^-, SCN^-, $S_2O_3^{2-}$
Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-	R_3P, R_3As, $(RO)_3P$
ROH, RO^-, R_2O	CN^-, RNC, CO
NH_3, RNH_2, N_2H_4	C_2H_4, C_6H_6
	H^-, R^-

Borderline
$C_6H_5NH_2$, C_5H_5N, N_3^-, Br^-, NO_2^-, SO_3^{2-}, N_2

Classification of Lewis Acids

Class (a)/Hard	Class (b)/Soft
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Cs^+
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}
Al^{3+}, Se^{3+}, Ga^{3+}, In^{3+}, La^{3+}	CH_3Hg^+
Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ir^{3+}	Tl^{3+}, $Tl(CH_3)_3$, RH_3
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Pu^{4+}, VO^{2+}	RS^+, RSe^+, RTe^+
UO_2^{2+}, $(CH_3)_2Sn^{2+}$	I^+, Br^+, HO^+, RO^+
$BeMe_2$, BF_3, BCl_3, $B(OR)_3$	I_2, Br_2, INC, etc.
$Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$	Trinitrobenzene, etc.
RPO_2^+,$ROPO_2^+$	Chloranil, quinones, etc.
RSO_2^+, $ROSO_2^+$, SO_3	Tetracyanoethylene, etc.
I^{7+}, I^{5+}, Cl^{7+}	O, Cl, Br, I, R_3C
R_3C^+, RCO^+, CO_2, NC^+	M^0 (metal atoms)
	Bulk metals
HX (hydrogen-bonding molelcules)	
Borderline	
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}	
$B(CH_3)_3$, SO_2, NO^+	