UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2014/2015

TITLE OF PAPER: INORGANIC CHEMISTRY

COURSE NUMBER: C301

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 TABLES 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) $[Co(urea)_6](ClO_4)_3$
iv) $(\eta^5\text{-}C_5H_5)_2Ti(OCH_2CH_3)_2$

[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:

i) $Ru(py)_3Cl_3$
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 energies on going from $[MnO_4]^-$ to $[MnO_4]^{2-}$

[6]

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

i) $[TiO(acac)_2]_2$, dimeric.

ii) $[(C_6F_5NCH_2CH_2)_3N]V$

[6]

c) Give an explanation for the fact that the complex $\{[CoNH_3)_6]\}_2\{[CoCl_4]\}_3$ has a room temperature magnetic moment of 3.71 BM. [Help: the compound is made up of two complex ions, one of which has a net charge of +3]

[6]

d) The treatment of an aqueous solution of $NiCl_2$ with two equivalents of $H_2NCH_2CH_2NH_2$ gives a blue complex (μ_{eff} 3.30 BM) which, on heating, loses two H_2O molecules per formula unit to form a yellow, diamagnetic compound. Suggest explanations for these observations.

[7]

Question Three

a) Comment on the following statements concerning electronic spectra

i) $[OsCl_6]^{3-}$ and $[RuCl_6]^{3-}$ exhibit LMCT bands at 282 and 348 nm respectively **[5]**

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

[4]

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]

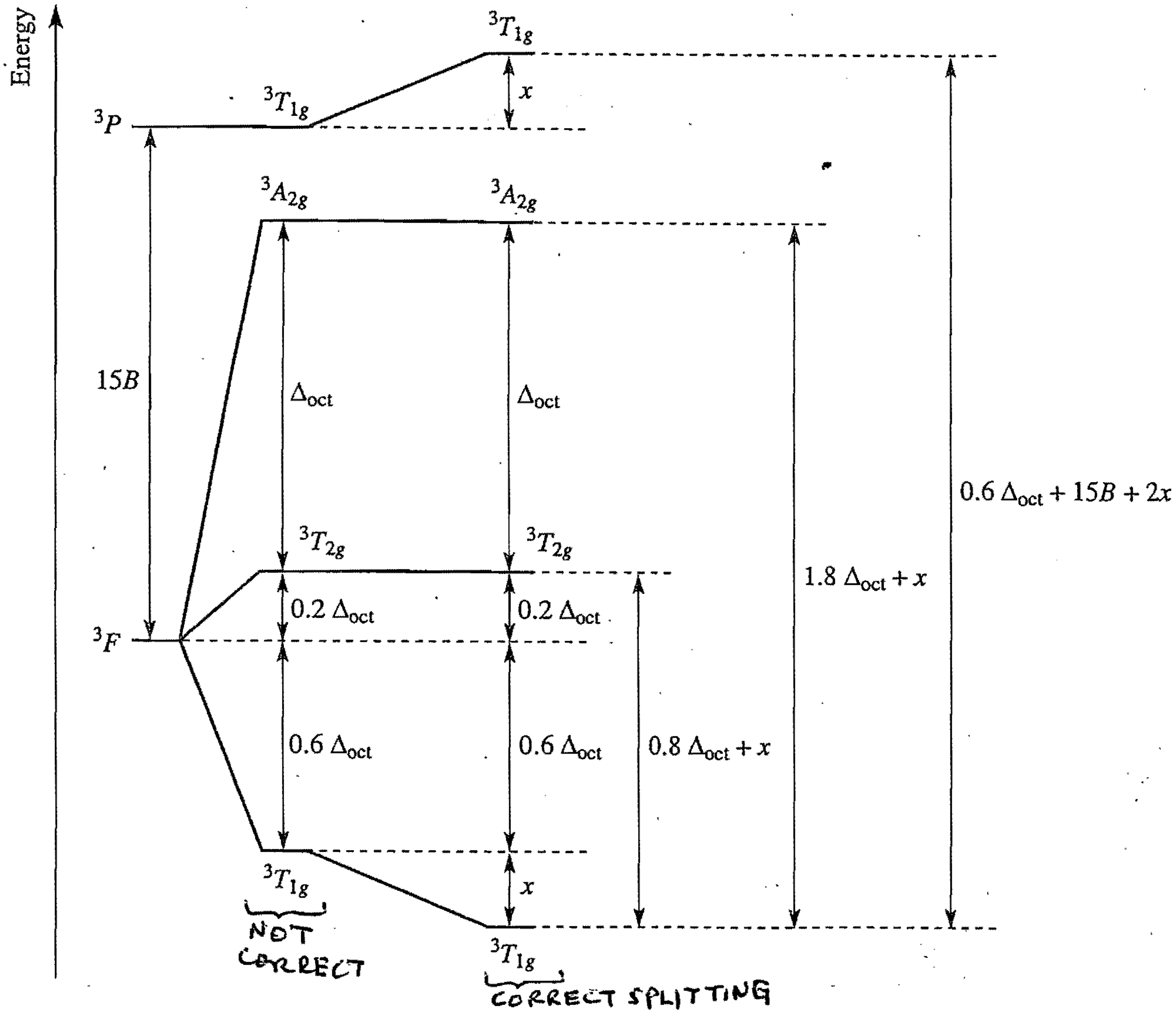


Diagram for Question 3 c)

Question Four

a) Complete and balance the following reactions:

i) $[CrO_4]^{2-}(aq) + H^+(aq) \rightleftarrows$
(in excess)

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

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

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

[8]

b) Draw one possible geometry for each of the following:

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

ii) CuCN, coordination no. =2

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

[6]

c) Explain each of the following:

i) $TiCl_4$ fumes when it is exposed to a moist atmosphere
ii) $[MnCl_6]^{2-}$ is unstable whereas $[MnF_6]^{2-}$ is quite stable
iii) CrO_3 is strongly oxidizing whereas WO_3 is very weakly oxidizing

[6]

d) Explain why Cu(I) compounds are diamagnetic irrespective of the coordination environment of the Cu(I) ion. However, they may exhibit colour, depending on the nature of the ligand

[5]

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]

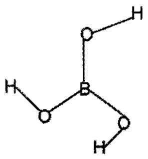
b) Consider the reaction

$$ML_nX + Y \longrightarrow ML_nY + X$$

where X is the leaving group and Y is the entering group. Use appropriate reaction equations to illustrate the two possible limiting mechanisms and sketch reaction profiles for each of the reaction pathways. The diagrams should be labeled, indicating reactants, intermediates (if any), etc. **[14]**

c) With the help of the flow-chart which is provided, determine the point group for the following:

Boric acid, $B(OH)_3$

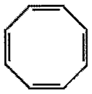


[3]

Question Six

a) With the help of the flow-chart which is provided, determine the point group for each of the following:

   i) C_8H_8



   ii) O=C=S

[6]

b) The complex ion, $[L_6M_2(\mu\text{-}X_2SO_2]^{2-}$, has four strong peaks in the IR spectrum, in the region between 900 and 1200 cm^{-1}. Two of the peaks are assigned to S-X stretching modes and the other two are assigned to S-O stretching modes. Show that these data are consistent with the "$\mu\text{-}X_2SO_2$" group having C_{2v} symmetry.

[13]

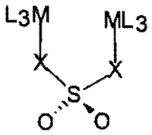


Diagram for Question 6(b)

c) From b) above, derive SALC's for S-O stretching modes and sketch the modes

`[6]

PERIODIC TABLE OF THE ELEMENTS

GROUPS

TRANSITION ELEMENTS

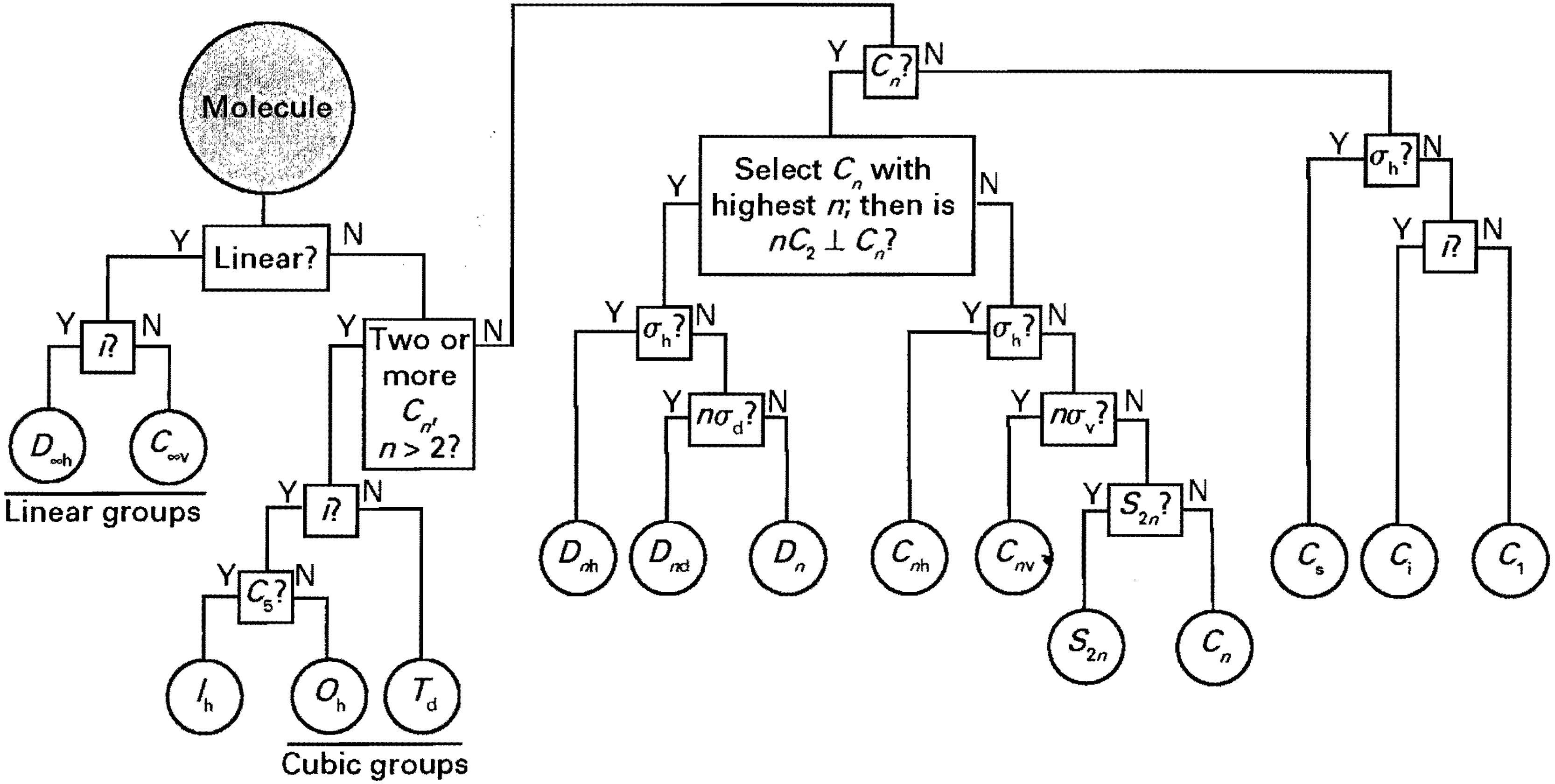
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
PERIODS	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 **H** 1																	4.003 **He** 2
2	6.941 **Li** 3	9.012 **Be** 4											10.811 **B** 5	12.011 **C** 6	14.007 **N** 7	15.999 **O** 8	18.998 **F** 9	20.180 **Ne** 10
3	22.990 **Na** 11	24.305 **Mg** 12											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.

The flow-chart (Decision tree) used for assigning point groups



Q. 6.

The C_{nv} Groups

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

EXAMPLES OF HARD, SOFT & BORDERLINE ACIDS & BASES

Type of Acid/Base	EXAMPLES
Hard acids	H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+} Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, Ir^{3+}, La^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, VO^{2+} , UO_2^{2+} $BeMe_2$, BF_3, BCl_3, $B(OR)_3$, $AlMe_3$
Soft acids	Cu^+, Ag^+, Au^+, Hg^+ , Cs^+ , Tl^+ , Hg^{2+} , Pd^{2+}, Cd^{2+} , Pt^{2+} Metal atoms in zero oxidation states
Border line acids	Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , $B(CH_3)_3$, SO_2, NO^+, BBr_3
Hard bases	H_2O, OH^-, F^-, Cl^-, CH_3CO_2-, PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, NO_3^-, ClO_4^-, ROH, RO^-, R_2O, NH_3, RNH_2, N_2H_4
Soft bases	RSH, RS^-, R_2S, I^-, CN^-, SCN^-, $S_2O_3^-$, R_3P, R_3As $(RO)_3P$, RNC, CO, C_2H_4, C_6H_6, R^-, H^-
Border line bases	Aniline, pyridine, N_3^-, Br^-, NO_2^-, SO_3^{2-}, N_2

From http://www.adichemistry.com/inorganic/cochem/hsab/hard-soft-acid-base-theory.html