UNIVERSITY OF SWAZILAND

FINAL EXAMINATION May 2018

TITLE OF PAPER: COORDINATION CHEMISTRY

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 OTHER USEFUL DATA HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

Question One

a) Name the following complexes:

(i) $[Co(C_2O_4)_3]^{3-}$

(ii) $[TaF_8]^{3-}$

[4]

b) Write formula for the following complexes:

(i) Dinitratotetraaminecobalt(III) sulphate

(ii) Trihydridotris(triphenylphosphine)ruthenium(III)

(iii) μ-hydroxobis[pentaamminechromium(III)] chloride

[6]

c) Show with drawings the enantiomorphs (i.e., optical isomers) of the "octahedral" complexes given below, where L-L is a bidentate ligand and X is a monodentate ligand.

i) $M(L\text{-}L)_2X_2$ ii) $M(L\text{-}L)_3$

[8]

d) Show how the experimental determination of the number of geometric isomers of $[Co(NH_3)_4Cl_2]^+$ would enable you to demonstrate that the coordination geometry is octahedral and not trigonal prismatic **[7]**

Question Two

a) With the help of suitable diagrams, explain how phosphines (R_3P) and phosphine oxides ($R_3P{=}O$) differ considerably in the way they function as ligands

[6]

b) Predict whether the equilibrium constant for each of the following reactions is expected to favour the forward reaction or the reverse reaction. Explain.

i) $CdI_2(s) + CaF_2(s) \rightleftharpoons CdF_2(s) + CaI_2(s)$

ii) $CaI_2(aq) + Cu_2O(s) \rightleftharpoons CaO(s) + 2CuI(s)$

iii) $HgCl_2(aq) + H_2S(aq) \rightleftharpoons HgS(s) + 2HCl(aq)$

[6]

c) Give two examples, together with Lewis strucures, of each of the following:

i) Monodentate ligands with oxygen as the donor atom

ii) Monodentate ligands with nitrogen as the donor atom

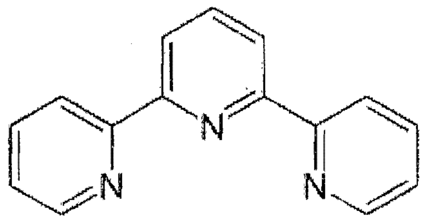
iii) Chelating ligands

iv) Macrocyclic ligands containing at least four N donor atoms

v) Crown ether ligands

[10]

d) Consider a ligand **L** whose structure is shown below.



Given that the formula of the complex is [Cu(CN)(**L**)], draw the structure of the complex.

[3]

Question Three

a) Which member of each pair would you expect to be more stable? Explain your answer:

i) $[PtCl_4]^{2-}$ or $[PtF_4]^{2-}$

ii) $[Al(H_2O)_6]^{3+}$ or $[Al(PR_3)_6]^{3+}$

iii) $Me_3B.PMe_3$ or $Me_3B.PC_6H_{11}$, C_6H_{11} = cyclohexyl radical

[6]

b) The following species have coordination numbers that are different from the ones suggested by their formulas. For each of the species, draw the structure that gives rise to the correct coordination number (given).

i) $[CuCl_3]^-$, CN=4)

ii) $[PtCl(NH_3)_2]^+$ CN=4

iii) CrF_5, CN=6

[6]

b) Calculate the CFSE for each of the two complexes, $[Mn(H_2O)_6]^{2+}$ and $[Co(CN)_6]^{3-}$. Justify your assumptions of high-spin or low-spin in each case.

[7]

c) Classify each of the following species as pi-acceptor or pi-donor ligands. For each case use suitable orbital diagrams to illustrate how π bonding between the ligand and a Lewis acid takes place.

i) N^{3-}, nitride

ii) CO, carbonyl ligand

[6]

Question Four

a) Copper(II) complexes are typically blue with one visible absorption band in their electronic spectra whereas copper(I) complexes are generally colourless. Explain. Assign spectroscopic labels to the states involved in the transition for an octahedral Cu^{2+} complex. Your answer should include electronic configurations of Cu(I) and Cu(II) ions.

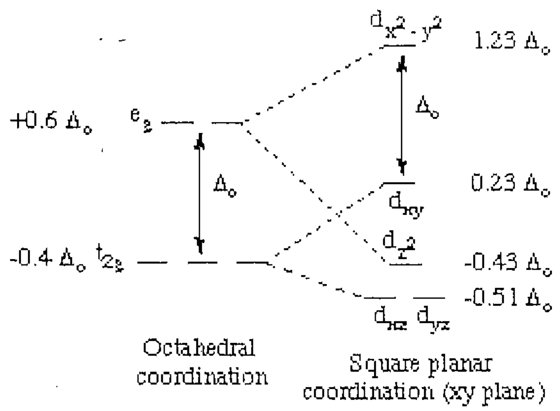
[10]

b) Aqueous solutions of $[Cr(C_2O_4)_3]^{3-}$ show absorptions at 17 400, and 23 600 cm^{-1} and a third band which occurs well into the ultraviolet. Use a suitable Tanabe-Sugano diagram to estimate values of B and Δ_o for the complex.

[10]

c) Complexes $[NiCl_2(PPh_3)_2]$ and $[PdCl_2(PPh_3)_2]$ are paramagnetic and diamagnetic, respectively. What does this tell you about their structures? With the help of the diagram given below, explain how you arrive at your answer.

[5]



Question Five

a) The pentacyanocobaltate(II) ion, $[Co(CN)_5]^{3-}$, is a catalyst for the conversion of $[Co(CN)_5\text{-}NCS]^{3-}$ (where NCS^- is N-bonded) to $[Co(CN)_5\text{-}SCN]^{3-}$ (where NCS^- is S-bonded) by an inner-sphere electron transfer mechanism. Show all the necessary steps for this reaction.

[10]

b) Consider intensities of absorption bands for isomers of a transition metal complex. Two isomers of an octahedral Co(III) complex, ML_4X_2, believed to be cis- and trans-isomers A and B respectively, give the following spectral features. Each of them gives two absorption bands in the visible region. The two bands of isomer A are symmetrical and poorly resolved with molar absorptivity,ε=60-80. Those of isomer B are of much lower intensity and well resolved. Draw structures of the two isomers and explain the differences in their spectral features.

[7]

c) Balance the following reactions:

i) $Cr_2O_3 + H_2SO_4$ (concd) →

ii) $Fe_2O_3 + HCl(g)$ →

iii) $Cr(s) + F_2(g)$→

iv) $W(s) + F_2(g)$ →

[8]

Question Six

a) Consider the elements Sc, Cr, Mn and Fe

i) Write the electron configuration for each of the elements **[8]**

ii) Give the group oxidation number for each element **[2]**

iii) Briefly, discuss the stability of group oxidation states for these elements.

[4]

iv) Titanium(IV) halides, TiX_4 (X=F, Cl, Br, I) have all been prepared. On the other hand, for manganese (IV), only MnF_4 has been prepared; preparation of the rest (X = Cl ,Br, I) has been unsuccessful. Explain. **[5]**

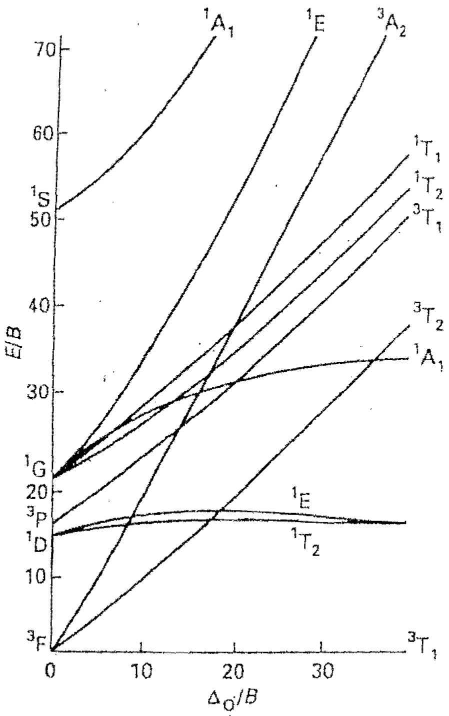
b) Consider a solution containing the followine ions: Hg^{2+}(aq), Cu^{+}(aq), Cr^{3+}(aq), and Fe^{3+}(aq). Give the resulting reaction equations (one for each) upon addition of an aqueous **basic** solution of sodium sulphide, Na_2S. [Note: An aqueous basic solution of a sulphide contains the ions OH^{-}(aq) and HS^{-}(aq)] **[6]**

END OF EXAMINATION

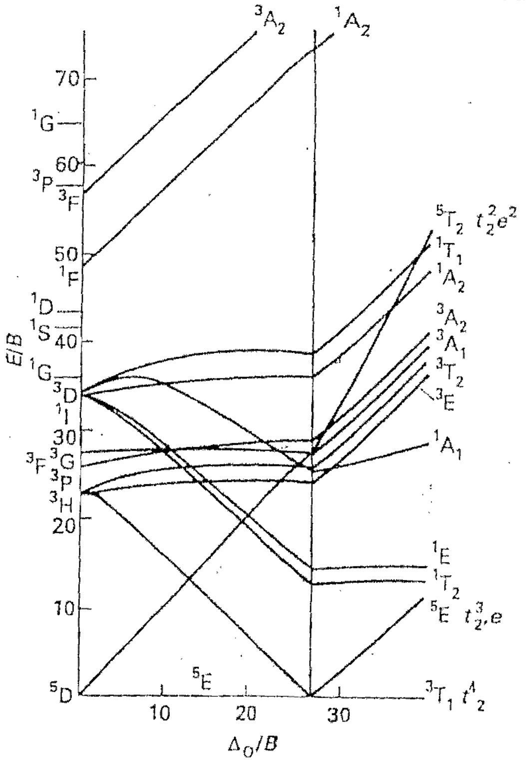
CHE322

1. d^2 with $C = 4.42B$

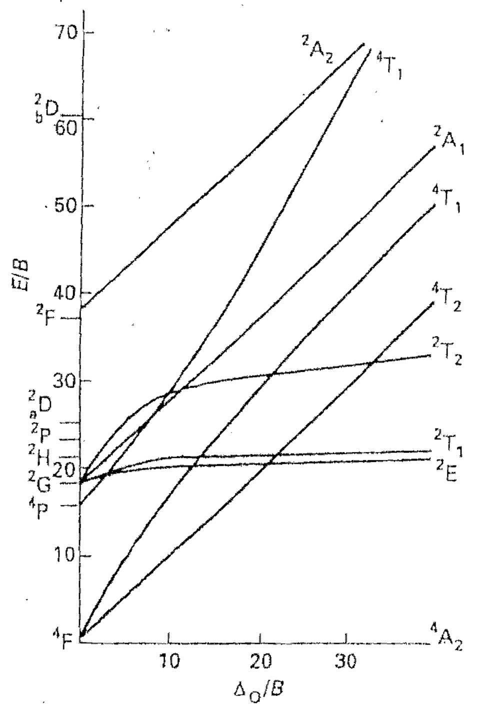
d^2



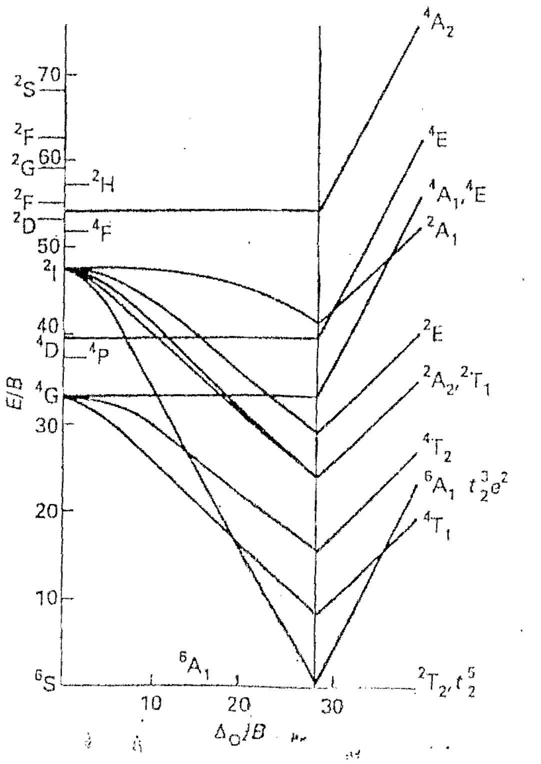
3. d^4 with $C = 4.61B$



2. d^3 with $C = 4.5B$



4. d^5 with $C = 4.477B$



CHE322

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.

CHE322 TABLES

TABLE 6-9
Hard and soft bases

Hard bases	*Borderline bases*	*Soft bases*
		H^-
F^-, (Cl^-)	Br^-	I^-
H_2O, OH^-, O^{2-}		H_2S, HS^-, S^{2-}
ROH, RO^-, R_2O, CH_3COO^-		RSH, RS^-, R_2S
NO_3^-, ClO_4^-	NO_2^-, N_3^-	SCN^-, CN^-, RNC, CO
CO_3^{2-}, SO_4^{2-}, PO_4^{3-}	SO_3^{2-}	$S_2O_3^{2-}$
NH_3, RNH_2, N_2H_4	$C_6H_5NH_2$, C_5H_5N, N_2	R_3P, $(RO)_3P$, R_3As
		C_2H_4, C_6H_6

SOURCE: Adapted from R. G. Pearson, *J. Chem. Educ.*, 1968, *45*, 581.

TABLE 6-10
Hard and soft acids

Hard acids	*Borderline acids*	*Soft acids*
H^+, Li^+, Na^+, K^+	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	$Co(CN)_5^{3-}$, Pd^{2+}, Pt^{2+}, Pt^{4+}
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}		
BF_3, BCl_3, $B(OR)_3$	$B(CH_3)_3$	BH_3, Tl^+, $Tl(CH_3)_3$
Al^{3+}, $Al(CH_3)_3$, $AlCl_3$, AlH_3		
Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}	GaH_3	$Ga(CH_3)_3$, $GaCl_3$, $GaBr_3$, GaI_3
Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{3+}	Rh^{3+}, Ir^{3+}, Ru^{3+}, Os^{2+}	Cu^+, Ag^+, Au^+, Cd^{2+}, Hg^+
		Hg^{2+}, CH_3Hg^+
CO_2, RCO^+, CH_3Sn^{3+}, $(CH_3)_2Sn^{2+}$	R_3C^+, $C_6H_5^+$, Sn^{2+}, Pb^{2+}	CH_2, carbenes
N^{3+}, RPO_2^+, $ROPO_2^+$, As^{3+}	NO^+, Sb^{3+}, Bi^{3+}	
SO_3, RSO_2^+, $ROSO_2^+$	SO_2	
Ions with oxidation states of 4 or higher		Br_2, I_2
HX (hydrogen-bonding molecules)		Metals with zero oxidation oxidation state
		π acceptors: trinitrobenzene, choroanil, quinones, tetracyanoethylene, etc.

SOURCE: Adapted from R. G. Pearson, *J. Chem. Educ.*, 1968, *45*, 581.

PHYSICAL CONSTANTS

Speed of light in a vacuum	c_0	2.99792458×10^8 m s^{-1}
Permittivity of a vacuum	ϵ_0	$8.854187816 \times 10^{-12}$ F m^{-1}
	$4\pi\epsilon_0$	1.11264×10^{-10} c^2 N^{-1} m^{-2}
Planck constant	h	$6.6260755(40) \times 10^{-34}$ J s
Elementary charge	e	$1.60217733(49) \times 10^{-19}$ C
Avogadro constant	N_A	$6.0221367(36) \times 10^{23}$ mol^{-1}
Boltzmann constant	k	$1.380658(12) \times 10^{-23}$ J K^{-1}
Gas constant	R	$8.314510(70)$ J K^{-1} mol^{-1}
Bohr radius	a_0	$5.29177249(24) \times 10^{-11}$ m
Rydberg constant	R_{∞}	1.0973731534[illegible] $\times 10^7$ m^{-1} (infinite nuclear mass)
	✓ R_H	1.09677759[illegible] $\times 10^7$ m^{-1} (proton nuclear mass)
Bohr magneton	μ_B	$9.2740154(31) \times 10^{-24}$ J T^{-1}
	π	3.14159265359
Faraday constant	F	$9.6485309(29) \times 10^4$ C mol^{-1}
Atomic mass unit	m_u	$1.6605402(10) \times 10^{-27}$ kg
Mass of the electron	m_e	$9.1093897(54) \times 10^{-31}$ kg or $5.48579903(13) \times 10^{-4}\ m_u$
Mass of the proton	m_p	$1.007276470(12)\ m_u$
Mass of the neutron	m_n	$1.008664904(14)\ m_u$
Mass of the deuteron	m_d	$2.013553214(24)\ m_u$
Mass of the triton	m_t	$3.01550071(4)\ m_u$
Mass of the α-particle	m_α	$4.001506170(50)\ m_u$