UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2013/2014

TITLE OF PAPER: INORGANIC CHEMISTRY I

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.

THE FOLLOWING HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER, AND ARE ATTACHED:

1. **Periodic Table**
2. **d^8 Tanabe-Sugano Diagram**
3. **Character Table for C_{2h} point group**
4. **Table of some hard, soft and intermediate acids and bases**
5. **Decision Tree**
6. **Table of Constants**

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

Question One

a) Name each of the following compounds:

i) $[Cr(NH_3)_6]^{3+}[Cr(CN)_6]^{3-}$
ii) $[Co(DMSO)_6]SO_4$
iii) $K_3[TiCl_6]$

[6]

b) Give the formula and draw **one possible** structure of each of the following:

i) Bis(acetyacetonato)oxovanadium(IV)
ii) Potassium tri-μ-chlorobis(trichloroferrate(III))

[8]

c) State the type of isomerism that may be exhibited by the following six-coordinate complexes, and draw structures of the isomers:

i) $Cr(py)_3Cl_3$, py= pyridine
ii) $Ru(dien)Br_3$, dien= $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2$

[11]

Question Two

a) When a solution of vanadate ion, VO_4^{3-}, is acidified with hydrochloric acid the complex ion, $[VO_2Cl_4]^{3-}$, is produced.

i) Deduce the oxidation number and the number of d electrons of the vanadium ion in the complex
ii) Write a balanced equation for the reaction
iii) Assuming octahedral geometry, give two possible isomers for the complex ion
iv) Use appropriate orbital diagrams to explain the nature of π bonding between the vanadium ion and any one of the oxo (i.e., O^{2-}) ligands.

[15]

b) The treatment of an aqueous solution of $NiCl_2$ with $H_2NCH(Ph)CH(Ph)NH_2$ gives a blue four-coordinate complex (μ_{eff} = 3.30 BM) which, upon heating, forms a yellow diamagnetic four-coordinate compound. Suggest explanations for these observations.

[10]

Question Three

a) Explain the following observations concerning electronic spectra

i) $[FeCl_4]^-$ and $[FeBr_4]^-$ exhibit LMCT bands at 220 and 244 nm respectively **[3]**

ii) $[CrO_4]^{2-}$ and $[MoO_4]^{2-}$ exhibit LMCT bands at 373 and 225 nm respectively **[3]**

iii) $[Fe(bpy)_3]^{2+}$ is expected to exhibit an MLCT band rather than an LMCT band **[3]**

b) The electronic spectra of $[V(H_2O)_6]^{3+}$, $[Ni(\mathbf{L_1})_6]^{2+}$, $[Ni(\mathbf{L_2})_3]^{2+}$ and $[Ni(\mathbf{L_3})_6]^{2+}$ show spin-allowed d-d absorption bands as shown in the table below.

Complex	Absorption band positions (cm^{-1})		
	v_1	v_2	v_3
$[V(H_2O)_6]^{3+}$	17400	25200	34500
$[Ni(\mathbf{L_1})_6]^{2+}$	10750	17500	28200
$[Ni(\mathbf{L_2})_3]^{2+}$	11000	18500	30000
$[Ni(\mathbf{L_3})_6]^{2+}$	8500	14000	25000

i) $\mathbf{L_1}$, $\mathbf{L_2}$ and $\mathbf{L_3}$ in Ni(II) complexes are three different ligands one of which is H_2O or NH_3 or en. Identify $\mathbf{L_1}$, $\mathbf{L_2}$ and $\mathbf{L_3}$. Explain your answer. **[5]**

ii) Use the **d^8 Tanabe-Sugano** diagram (attached) to identify the transitions that correspond to the bands (v_1, v_2, v_3) belonging to Ni(II) complexes. **[4]**

iii) Use the **d^8 Tanabe-Sugano** diagram (attached) to identify the transitions that correspond to the bands (v_1, v_2, v_3) belonging to V(III) aqua complex. **[5]**

iv) Among the three Ni(II) complexes, which one is expected to exhibit the most intense absorption bands? Explain your answer. **[2]**

Question Four

a) Complete and balance the following reactions:

i) $[Cr(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftarrows$

ii) $Fe + Cl_2 \longrightarrow$

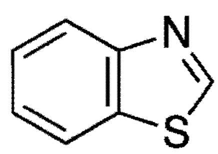
iii) $Fe + I_2 \longrightarrow$

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

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

[10]

b) Reaction of mercury(II) iodide, HgI_2, with benzothiazole leads to the formation of a complex of formula $HgI_2.L_2$, where L=benzothiazole. The structure of benzothiazole is shown below. Give sketches of three isomers that the complex may exhibit. Which isomer is expected to be the most stable? Explain your answer. **[7]**



c) The common minerals of copper and nickel contain copper sulphides and nickel sulphides. In contrast, aluminium is obtained from the oxide, Al_2O_3, and calcium from the the carbonate, $CaCO_3$. Can these observations be explained in terms of hardness? Explain. **[4]**

d) Of the metals cadmium, chromium, lead, strontium and palladium, which might be expected to occur in mineral form as oxides and which as sulphides, and which as oxides or sulphides? Explain

[4]

Question Five

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

i) Anation reaction
ii) Self-exchange electron transfer reaction

[6]

b) Consider the reaction

$$ML_xX + Y \longrightarrow ML_xY + X$$

where X is the leaving group and Y is the entering group. Use appropriate reaction equations to illustrate the two possible limiting mechanisms.

[4]

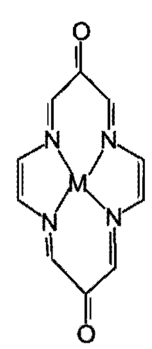
c) Give expressions for the two principal sets of equilibrium constants (K_i's and β_i's) for the formation of a series of complexes $[M(H_2O)_3L]^{2+}$, $[M(H_2O)_2L_2]^{2+}$, and $[M(H_2O)L_3]^{2+}$ (in aqueous solution) starting with $[M(H_2O)_4]^{2+}$, where L is a monodentate neutral ligand. How are K_i's related to β_i's for i=1, 2, 3, 4?

[15]

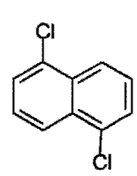
Question Six

a) With the help of the "Decision Tree" which is provided, determine the point group for each of the following:

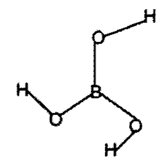
i)



ii) 1,5-dichloronaphthalene

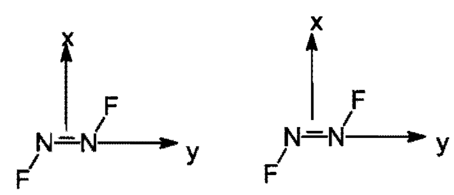


iii) Boric acid, $B(OH)_3$



[9]

b) Consider *trans*-N_2F_2. The molecule has a planar nonlinear structure as shown below. It belongs to the point group C_{2h}. [Note: The z axis is perpendicular to the xy plane which coincides with the molecular plane. Also the z axis coincides with C_2 axis].



Let the two N-F bond stretches (r_1 and r_2) constitute one basis set and let the N=N bond stretch (r_3) constitute another basis set. Now answer the questions that follow.

i) Determine the reducible representation arising from the basis set (r_1, r_2). Then determine the symmetries of the corresponding stretching (N-F) vibrational modes

ii) Apply the same procedure as in i) to the basis set (r_3).

iii) Which of the bands are both IR active active and Raman active.

iv) Derive the SALCs for each of the vibrational modes in i) and ii) above, and sketch the results.

[16]

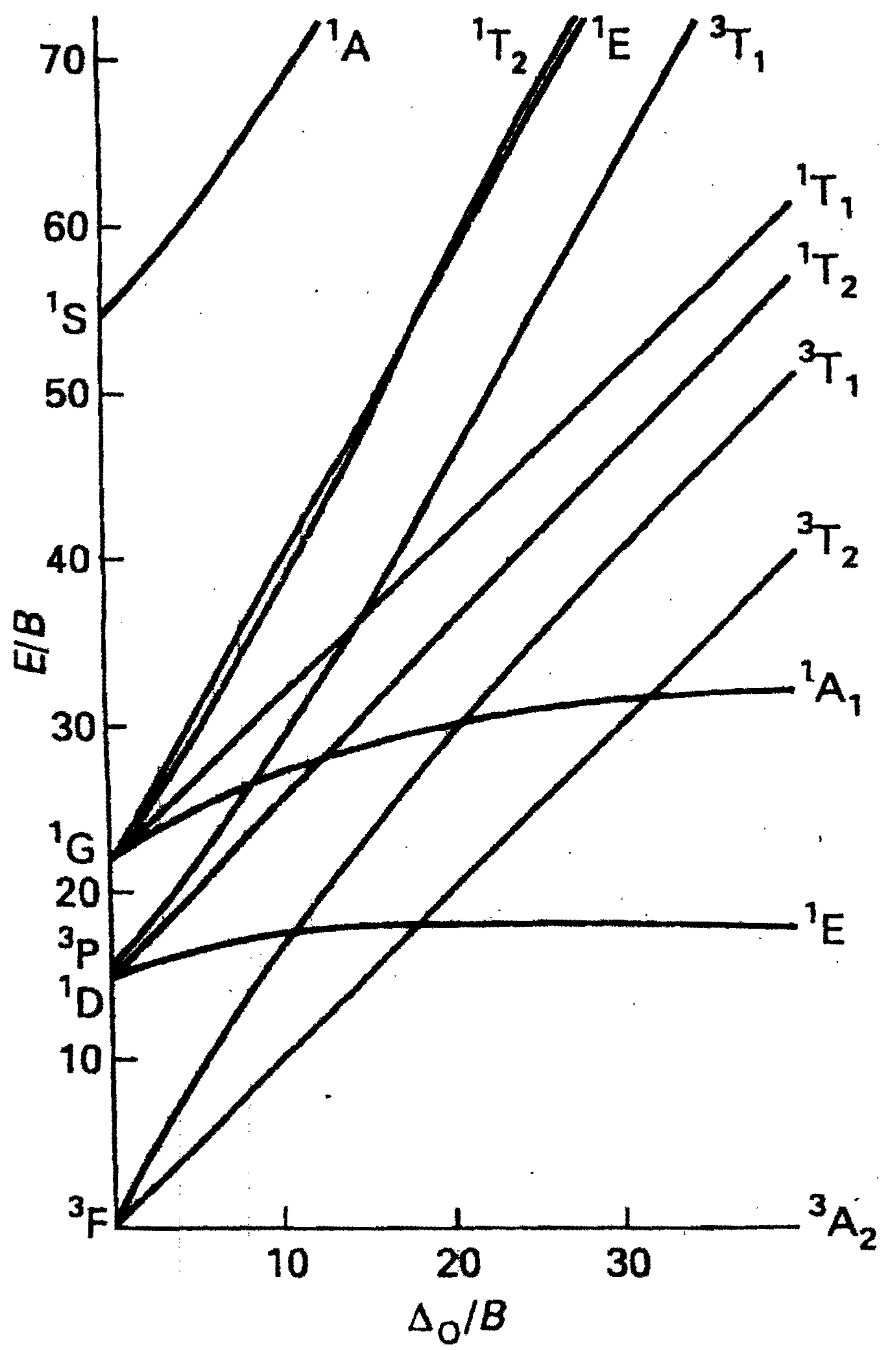
Table of hard, intermediate and soft Acids and Bases

	Ligands (Lewis bases)	Metal centres (Lewis acids)
Hard; class (a)	F^-, Cl^-, H_2O, ROH, R_2O, $[OH]^-$, $[RO]^-$, $[RCO_2]^-$, $[CO_3]^{2-}$, $[NO_3]^-$, $[PO_4]^{3-}$, $[SO_4]^{2-}$, $[ClO_4]^-$, $[ox]^{2-}$, NH_3, RNH_2	Li^+, Na^+, K^+, Rb^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Y^{3+}, Th^{4+}, Pu^{4+}, Ti^{4+}, Zr^{4+}, $[VO]^{2+}$, $[VO_2]^+$
Soft; class (b)	I^-, H^-, R^-, $[CN]^-$ (*C*-bound), CO (*C*-bound), RNC, RSH, R_2S, $[RS]^-$, $[SCN]^-$ (*S*-bound), R_3P, R_3As, R_3Sb, alkenes, arenes	Zero oxidation state metal centres, Tl^+, Cu^+, Ag^+, Au^+, $[Hg_2]^{2+}$, Hg^{2+}, Cd^{2+}, Pd^{2+}, Pt^{2+}, Tl^{3+}
Intermediate	Br^-, $[N_3]^-$, py, $[SCN]^-$ (*N*-bound), $ArNH_2$, $[NO_2]^-$, $[SO_3]^{2-}$	Pb^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Os^{2+}, Ru^{3+}, Rh^{3+}, Ir^{3+}

Character Table for C_{2h} Point Group

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y	xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	

d^8 Tanabe-Sugano Diagram



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_∞	$1.0973731534(13) \times 10^{7}$ m^{-1} (infinite nuclear mass)
	✓ R_H	$1.09677759(50) \times 10^{7}$ 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

PERIODIC TABLE OF THE 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	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.

DECISION TREE