UNIVERSITY OF SWAZILAND

CHEMISTRY DEPARTMENT

SUPPLEMENTARY EXAMINATION 2018

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 USEFUL DATA HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

Question One

a) Name the following complexes:

(i) $[FeO_4]^{2-}$

(ii) $K_4[V(CN)_7].2H_2O$

(iii) $NiBr_3(PPh_3)_2$

[6]

b) Write a possible and reasonable structure for each of the following complexes:

(i) Carbonatopentaamminecobalt(III) chloride

(ii) Di-μ-acetatobis[diammineplatinum(II) chloride

iii) Potassium tetrabromocuprate(II)

[9]

c) Consider a complex ML_6 where L is a monodentate ligand. Give sketches of four possible geometries that can be adopted by such a complex.

[10]

Question Two

(a) Draw a structure for each of the following compounds or ions:

(i) *mer*- bis(acetonitrile)trichlorooxoniobium(V), where acetonitrile = CH_3CN

(ii) di-μ-hydroxobis[bis(ethylenediamine)chromium(III)]

[5]

b) Determine the oxidation state and number of d electrons for the metal in each of the complexes:

(i) $[Fe(CN)(CO)_4]^-$

(ii) $[NiBr_3(PEt_3)_2]$

[6]

c) Consider the compounds $[Pt(NH_3)_4]SO_4$ and $Ag_2[PtCl_4]$. Describe chemical methods by which they can be distinguished from each other.

[4]

d) Consider a complex corresponding to the formula $[Cr(SCN)(H_2O)_5]Br.2H_2O$.

i) Sketch the structures of linkage isomers of the cation in the complex
ii) Give the formulas of ionization isomers of the *compound*
(v) Give the formulas of **two** hydrate isomers of the *compound*

[10]

Question Three

a) Explain each of the following:

i) The manganous ion, $[Mn(H_2O)_6]^{2+}$, reacts with CN^- to form $[Mn(CN)_6]^{4-}$ which has a magnetic moment (μ) of 1.95 B.M., but reacts with I^- to give $[MnI_4]^{2-}$ which has μ =5.93 B.M.

ii) $[PtBr_2Cl_2]^{2-}$ exists in two isomeric forms, whereas $[NiBr_2Cl_2]^{2-}$ does not exhibit isomerism.

[11]

c) Give examples of macrocyclic ligands containing as donor atoms

i) oxygen only
ii) nitrogen only
iii) sulphur only

[6]

d) Describe how pi-donor and pi-acceptor ligands can stabilize high or low oxidation states of transition metal ions. To illustrate your answer, give one example for each type of such ligands.

[8]

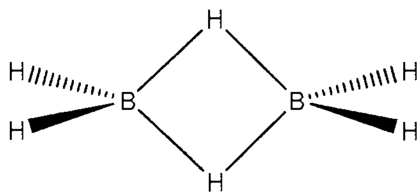
Question Four

a) Give the relevant selection rules for electronic transitions in spectra of transition metal complexes. What factors can lead to their relaxation?

[8]

b) List and identify by location all the symmetry elements present in the B_2H_6 molecule. Then determine the correct point group for the molecule. The structure of the molecule is sketched below.

[4]



c) A four-coordinate Pd(II) complex, $[Pd(CO)_2Cl_2]$, is believed to be square planar in coordination geometry. *Trans*-square planar coordination would have D_{2h} symmetry, while *cis*-square planar coordination has C_{2v} symmetry.

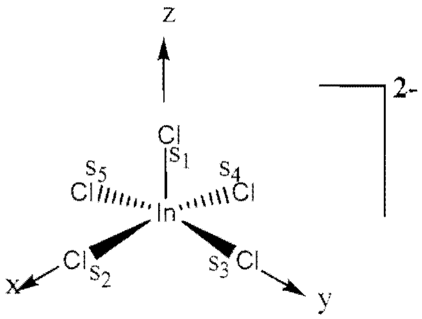
i) Draw structures the two possible isomers

ii) Work out the symmetry-allowed IR and Raman v(Pd-Cl) bands for the *trans* isomer (D_{2h} symmetry)

[13]

Question Five

Consider the square pyramidal complex, $[InCl_5]^{2-}$, whose structure is sketched below. Let s_1, s_2, s_3, s_4 and s_5 represent ligand σ-type (sigma-type) orbitals.



a) Given that the point group of the complex is C_{4v}, generate a reducible representation of the ligand sigma-type orbitals and decompose it into irreducible representations. **[13]**

c) From the results obtained in a) and b) above, create a table with column headings as shown below. For each irreducible representation, Γ_σ, of the ligand s orbitals, list matching atomic orbital(s) on the In atom.

[6]

Irreducible representation, Γ_σ, from ligand sigma-type orbitals,	Valence atomic orbital(s) on central atom, In

d) Using the data in c) above, give four possible hybridization schemes for bonding between ligand orbitals and valence orbitals on the In(III) center.

[6]

Question Six

a) Using hard-soft concepts, figure out in which direction, forward or reverse, the following reactions are expected to be more favourable:

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

ii) $[CuI_4]^{2-} + [CuCl_4]^{3-} \longrightarrow [CuCl_4]^{2-} + [CuI_4]^{3-}$

[8]

b) Consider the ligand $H_2N\text{-}CH_2\text{-}P(CH_3)_2$ which has two donor atoms, P and N. Decide which donor atom is more likely to bind to boron in each complex with the formulas as shown below. Explain your answer.

i) BH_3 ii) BF_3

[3]

e) Considering the concept of hard acids and bases, state two essential characteristics of each of the following:

i) hard acids

ii) soft acids

[4]

d) Give balanced reaction equations depicting the reaction of transition metals with non-metals as shown below.

i) $Cr(s) + O_2(g) \rightarrow$

ii) $W(s) + O_2(g) \rightarrow$

iii) $Mn(s) + Cl_2(g) \rightarrow$

iv) $Ti(s) + Cl_2(g) \rightarrow$

v) $V(s) + Cl_2(g) \rightarrow$

[10]

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											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									

TRANSITION ELEMENTS

* 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 = 1.097×10^7 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 = 1.01325×10^5 Pa
= 760 torr
1 bar = 1×10^5 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 = 1.602×10^{-19} J

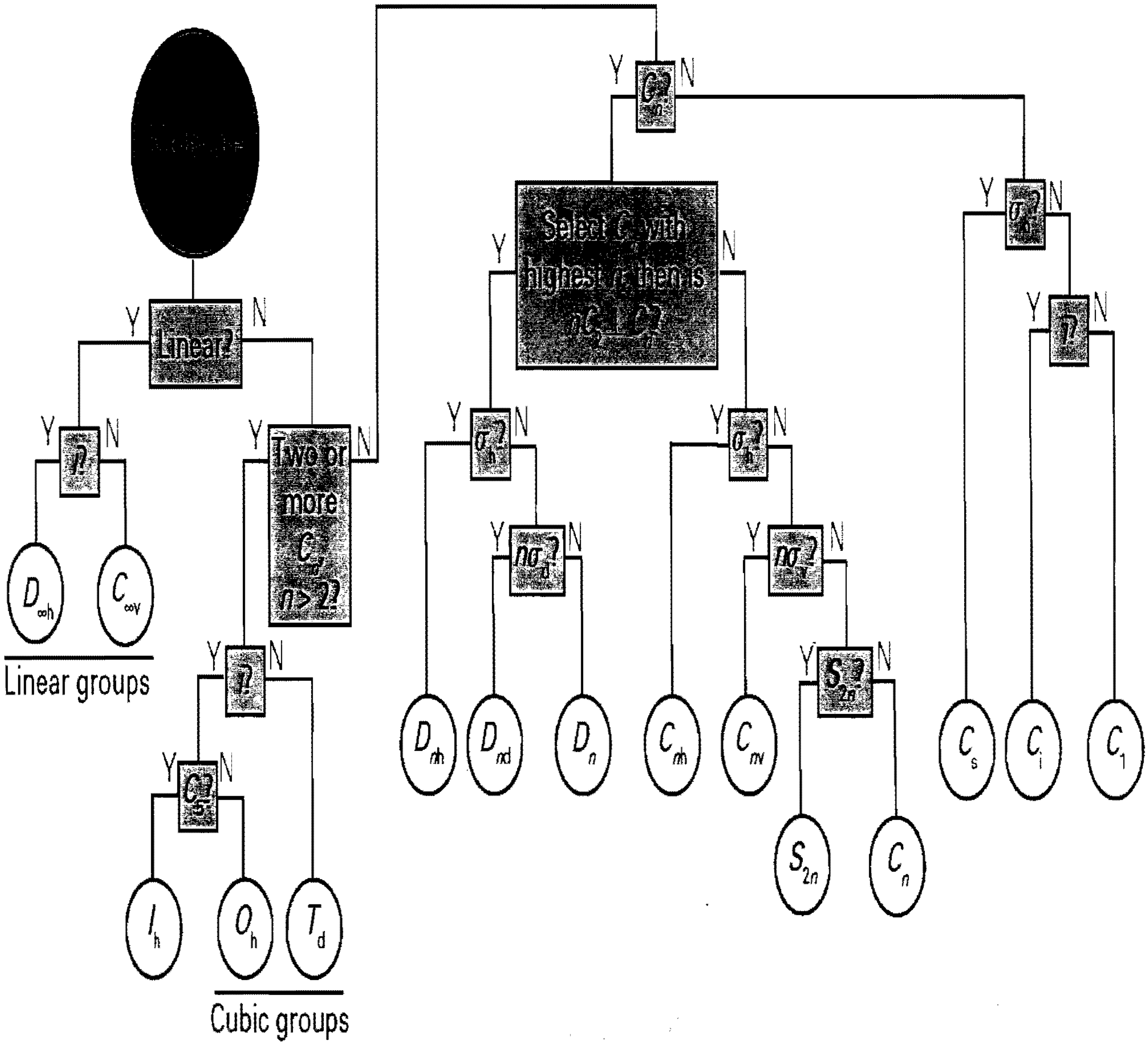
Math relationships

$\pi = 3.1416$
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

C301 Decision Tree (Flow Chart)



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

C301

Character tables for point groups C_{4v} and D_{2h}

C_{4v}	E	$2C_4$ (z)	C_2	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	+1	z	x^2+y^2, z^2	z^3, $z(x^2+y^2)$
A_2	+1	+1	+1	-1	-1	R_z	-	-
B_1	+1	-1	+1	+1	-1	-	x^2-y^2	$z(x^2-y^2)$
B_2	+1	-1	+1	-1	+1	-	xy	xyz
E	+2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)	(xz^2, yz^2) (xy^2, x^2y) (x^3, y^3)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

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^+	