

UNIVERSITY OF SWAZILAND
SUPPLEMENTARY 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 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.**

Question One

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

- i) $K_3[Co(NO_2)_6]$
- ii) $[Cr(en)_3]^{3+}[Cr(Ox)_3]^{3-}$
- iii) $[Cl_3W(\mu-Cl)_3WCl_3](ClO_4)_3$
- iv) $W(CH_2CH_3)_6$

[6]

b) Give the formula of each of the following:

- i) Sodium pentacyanonitrosylferrate(II) dihydrate
- ii) Potassium pentachloronitrosmate(IV)
- iii) Tetraammineaquacobalt(III)- μ -cyanobromotetracyanocobaltate(III)

[6]

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

- i) $[Pt(en)_2Cl_2]Br_2$
- ii) $Pd(bpy)(NCS)_2$
- iii) $RhH_3(PPh_3)_3$

[13]

Question Two

a) A monomeric complex of cobalt gave the following result on analysis:

Species	Co	NH ₃	Cl ⁻	SO ₄ ²⁻	H ₂ O
%, by mass	21.24	24.77	12.81	34.65	?

The compound is diamagnetic and contains no other groups or elements, except that water might be present.

- i) Using the above data, calculate the formula of the compound
- ii) Check if there is any water present. If water is present, what is the final formula of the compound?

[8]

b) The magnetic moment for the complex $[CoF_6]^{3-}$ is found to be 5.63 BM. Explain why this value does not agree with the value of magnetic moment calculated from the spin-only formula.

[6]

- c) Explain why under the influence of an octahedral field, the energies of the d orbitals are raised or lowered.

[7]

- d) What is the expected ordering of Δ_o for $[\text{Fe}(\text{OH}_2)_6]^{2+}$, $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$? Rationalize your answer.

[4]

Question Three

- a) A reaction of *trans*- $[\text{Pt}(\text{PEt}_3)_2(\text{Ph})\text{Cl}]$ with thiourea, tu, in methanol follows a two-term rate law with

$$k_{\text{obs}} = k_1 + k_2[\text{tu}]$$

Give a plausible mechanism for the reaction. Suggest how the values of k_1 and k_2 may be obtained.

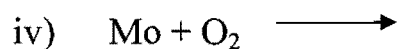
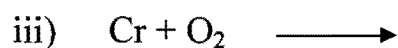
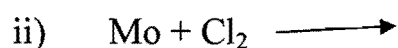
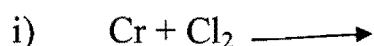
[8]

- b) $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ has absorption bands at 17800, 25700 and 34500 cm^{-1} . Using the Tanabe-Sugano diagram for a d^2 configuration, estimate values of Δ_o and B for this complex.

[17]

Question Four

- a) Complete and balance the following reactions:



[8]

- b) Sketch at least three possible geometries for a complex with coordination number six (CN=6).

[6]

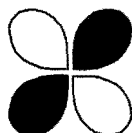
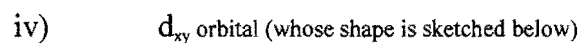
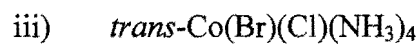
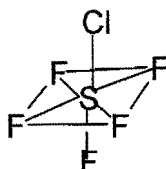
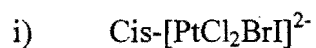
- c) Explain each of the following:
- i) TiO_2 is white but TiCl_3 is violet [4]
 - ii) Iron(VI) oxide is more oxidizing than chromium(VI) oxide. [4]
- e) Write equations to show the reaction of Cr_2O_3 with sulfuric acid [3]

Question Five

- a) Starting with $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ and chloride ion, Cl^- , suggest a method for preparing each of the following:
- i) *trans*- $[\text{RhCl}_2(\text{H}_2\text{O})_4]^+$
 - ii) *mer*- $[\text{RhCl}_3(\text{H}_2\text{O})_3]$
 - iii) *trans*- $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$
- [7]
- b) The electronic spectrum of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ has one peak which is around 1000 nm. On the other hand, the complex $[\text{Fe}(\text{CN})_6]^{4-}$ exhibits at least two absorption bands at lower wave lengths. By using the appropriate Tanabe-Sugano diagram, account for the likely origin of the absorption bands for each of the complexes. [8]
- c) Discuss, with examples (one for each), the difference between outer-sphere and inner-sphere mechanisms. State what is meant by a self-exchange mechanism. [7]
- d) What reason can you suggest for the sequence $\text{Co} > \text{Rh} > \text{Ir}$ in the rates of H_2O exchange of $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ ions? [3]

Question Six

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



[12]

b) Determine the symmetries of Cr-O stretching modes for the complex $[\text{CrO}_3\text{X}]^-$ (which has C_{3v} point group). Which ones of the modes are IR active? Which ones are Raman active? Show all your work.

[13]

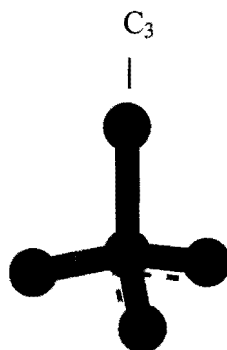


Table of hard, intermediate and soft Acids and Bases

	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 TABLES

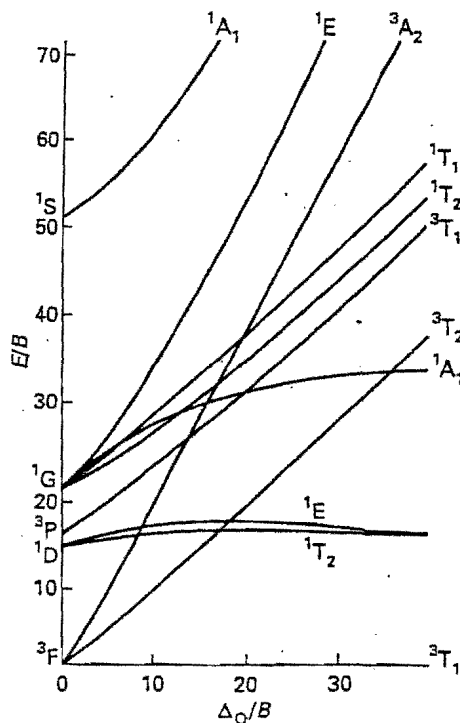
4. The C_{np} Groups

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_x	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

TANABE-SUGANO DIAGRAMS

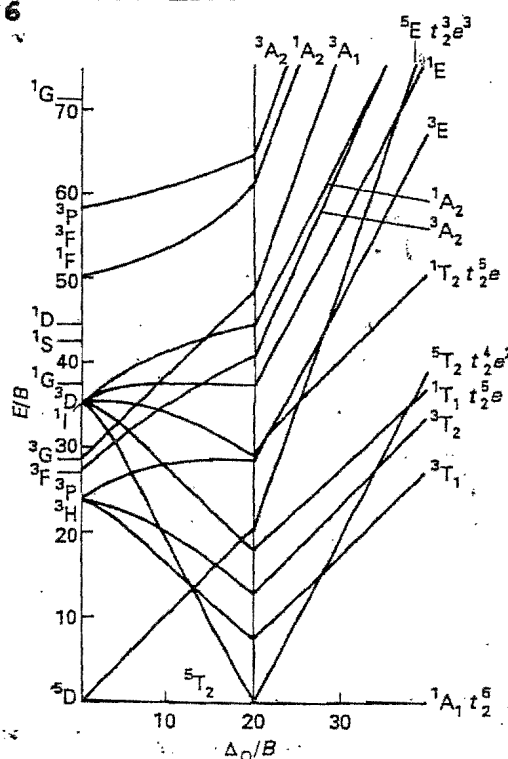
 d^2 with $C = 4.42B$

2



d^6 with $C = 4.8B$

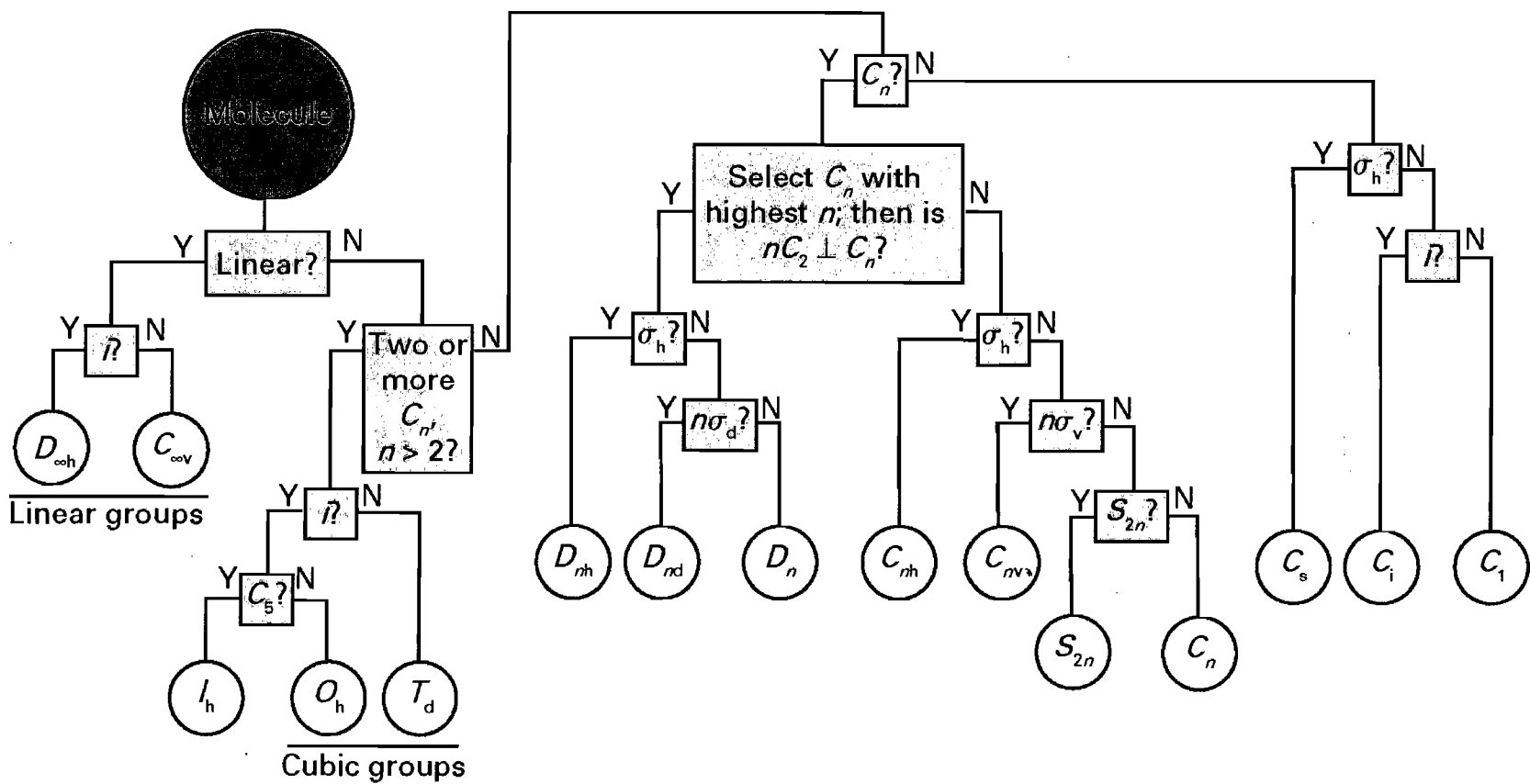
46



PHYSICAL CONSTANTS

Speed of light in a vacuum	c_0	$2.99792458 \times 10^8 \text{ m s}^{-1}$
Permittivity of a vacuum	ϵ_0	$8.854187816 \times 10^{-12} \text{ F m}^{-1}$
	$4\pi\epsilon_0$	$1.11264 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$
Planck constant	h	$6.6260755(40) \times 10^{-34} \text{ J s}$
Elementary charge	e	$1.60217733(49) \times 10^{-19} \text{ C}$
Avogadro constant	N_A	$6.0221367(36) \times 10^{23} \text{ mol}^{-1}$
Boltzmann constant	k	$1.380658(12) \times 10^{-23} \text{ J K}^{-1}$
Gas constant	R	$8.314510(70) \text{ J K}^{-1} \text{ mol}^{-1}$
Bohr radius	a_0	$5.29177249(24) \times 10^{-11} \text{ m}$
Rydberg constant	R_∞	$1.0973731534(13) \times 10^7 \text{ m}^{-1}$ (infinite nuclear mass)
	R_H	$1.096777 \times 10^7 \text{ m}^{-1}$
Bohr magneton	μ_B	$9.2740154(31) \times 10^{-24} \text{ J T}^{-1}$
	π	3.14159265359
Faraday constant	F	$9.6485309(29) \times 10^4 \text{ C mol}^{-1}$
Atomic mass unit	m_u	$1.6605402(10) \times 10^{-27} \text{ kg}$
Mass of the electron	m_e	$9.1093897(54) \times 10^{-31} \text{ kg}$ 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	$4.001506170(50) m_u$

The flowchart is a decision tree for determining the point group of a molecule. It starts with a 'Molecule' node, which leads to a 'Linear?' decision box. If 'Linear?' is 'Y', it leads to a ' ∞ ' decision box. If ' ∞ ' is 'Y', it leads to the $D_{\infty h}$ node. If ' ∞ ' is 'N', it leads to the $C_{\infty v}$ node. These two nodes are grouped under 'Linear groups'. If 'Linear?' is 'N', it leads to a 'Two or more C_n , $n > 2$?' decision box. If 'Y', it leads to a ' ∞ ' decision box. If ' ∞ ' is 'Y', it leads to a ' C_5 ?' decision box. If ' C_5 ?' is 'Y', it leads to the I_h node. If ' C_5 ?' is 'N', it leads to the O_h node. If ' ∞ ' is 'N', it leads to the T_d node. These three nodes are grouped under 'Cubic groups'. If 'Two or more C_n , $n > 2$?' is 'N', it leads to a 'Select C_n with highest n ; then is $nC_2 \perp C_n$?' decision box. If 'Y', it leads to a ' σ_h ?' decision box. If ' σ_h ?' is 'Y', it leads to the D_{nh} node. If ' σ_h ?' is 'N', it leads to a ' $n\sigma_d$?' decision box. If ' $n\sigma_d$?' is 'Y', it leads to the D_{nd} node. If ' $n\sigma_d$?' is 'N', it leads to the D_n node. If 'Select C_n with highest n ; then is $nC_2 \perp C_n$?' is 'N', it leads to a ' σ_h ?' decision box. If ' σ_h ?' is 'Y', it leads to the C_{nh} node. If ' σ_h ?' is 'N', it leads to a ' $n\sigma_v$?' decision box. If ' $n\sigma_v$?' is 'Y', it leads to the C_{nv} node. If ' $n\sigma_v$?' is 'N', it leads to a ' S_{2n} ?' decision box. If ' S_{2n} ?' is 'Y', it leads to the S_{2n} node. If ' S_{2n} ?' is 'N', it leads to the C_n node. The flowchart also includes a branch from the 'Molecule' node to a ' C_n ?' decision box. If ' C_n ?' is 'Y', it leads to the 'Select C_n with highest n ; then is $nC_2 \perp C_n$?' decision box. If ' C_n ?' is 'N', it leads to a ' σ_h ?' decision box. If ' σ_h ?' is 'Y', it leads to the C_s node. If ' σ_h ?' is 'N', it leads to a ' ∞ ' decision box. If ' ∞ ' is 'Y', it leads to the C_i node. If ' ∞ ' is 'N', it leads to the C_1 node.



1 1A											13 3A	14 4A	15 5A	16 6A	17 7A	18 8A			
1 H Hydrogen 1.008	2 2A											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18		
3 Li Lithium 6.941	4 Be Beryllium 9.012	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.07	17 Cl Chlorine 35.45	18 Ar Argon 39.95		
11 Na Sodium 22.99	12 Mg Magnesium 24.31	19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.39	31 Ga Gallium 69.72	32 Ge Germanium 72.59	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.1	45 Rh Rhodium 102.9	46 Pd Palladium 106.4	47 Ag Silver 107.9	48 Cd Cadmium 112.4	49 In Indium 114.8	50 Sn Tin 118.7	51 Sb Antimony 121.8	52 Te Tellurium 127.6	53 I Iodine 126.9	54 Xe Xenon 131.3		
55 Cs Cesium 132.9	56 Ba Barium 137.3	57 La Lanthanum 138.9	72 Hf Hafnium 178.5	73 Ta Tantalum 180.9	74 W Tungsten 183.9	75 Re Rhenium 186.2	76 Os Osmium 190.2	77 Ir Iridium 192.2	78 Pt Platinum 195.1	79 Au Gold 197.0	80 Hg Mercury 200.6	81 Tl Thallium 204.4	82 Pb Lead 207.2	83 Bi Bismuth 209.0	84 Po Polonium (210)	85 At Astatine (210)	86 Rn Radon (222)		
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (257)	105 Db Dubnium (260)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 Ds Darmstadtium (269)	111 Rg Roentgenium (272)	112	(113)	114	(115)	116	(117)	(118)		

	Metals	58 Ce Cerium 140.1	59 Pr Praseodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium (147)	62 Sm Samarium 150.4	63 Eu Europium 152.0	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 175.0
	Metalloids														
	Nonmetals	90 Th Thorium 232.0	91 Pa Protactinium (231)	92 U Uranium 238.0	93 Np Neptunium (237)	94 Pu Plutonium (242)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (249)	99 Es Einsteinium (254)	100 Fm Fermium (253)	101 Md Mendelevium (256)	102 No Nobelium (254)	103 Lr Lawrencium (257)

The 1–18 group designation has been recommended by the International Union of Pure and Applied Chemistry (IUPAC) but is not yet in wide use. In this text we use the standard U.S. notation for group numbers (1A–8A and 1B–8B). No names have been assigned for elements 112, 114, and 116. Elements 113, 115, 117, and 118 have not yet been synthesized.

C301 NOTES

