UNIVERSITY OF SWAZILAND

FINAL EXAMINATIONS

ACADEMIC YEAR 2017/2018

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.

THE FOLLOWING HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER:

- Periodic Table of the Elements
- Table of Universal Constants
- Table of Hard and Soft Acids and Bases
- Tanabe-Sugano diagrams for octahedral complexes
- Character tables for C_{2v} and D_{3h} point groups

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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) Give the IUPAC name for each of the following:

i) $Na_2[Cd(CN)_4]$
ii) $[Cr(NH_3)_6][Cr(CN)_6]$
iii) $[Co(NH_3)_4(H_2O)Br]Br$

[6]

b) Give the formula of each of the following:

i) Sodium pentacyanonitrosylferrate(II) dihydrate
ii) Potassium pentachloronitridoosmate(IV)
iii) Tetraamminеaquacobalt(III)-μ-cyanobromotetracyanocobaltate(III)

[6]

c) Briefly discuss the observed trends in the stability of oxidation states across the periods from left to right and down the groups of the transition metal elements. Use examples to illustrate your answer.

[6]

d) What is the ***chelate effect***? Give two ways of explaining how the chelate effect leads to greater stability of complexes.

[7]

Question Two

a) Sketch the structures of all possible isomers that may arise from the complexes given below. If appropriate, distinguish delta from lambda isomer(s).

i) $[Ni(SCH_2CH_2NH_2)_2]$, square planar
ii) $[Co(en)_3]^{3+}$ [9]

b) For each of the following complexes, give the oxidation state of the metal and its d^N configuration.

i) $[Mn(CN)_6]^{4-}$
ii) $[Cr(acac)_3]$ [4]

c) What is the "hole formalism"? Give two examples to illustrate your answer.

[4]

d) Explain the origins of LMCT absorptions in the electronic spectra of d-block metal complexes. Give two examples to illustrate your answer. [8]

Question Three

a) For each of the complexes given below, determine the oxidation number and electron configuration, d^N, of the transition metal ion.

i) $Mg[MoO_4]$

ii) $[Fe(CO)_4]^{2-}$

[6]

b) Write balanced chemical equations for

i) Reaction of $TiCl_4$ with water

ii) Air oxidation of Fe^{3+}

iii) Reaction of CrO_3 with potassium hydroxide.

iv) Addition I- to aqueous F^{3+}

[8]

c) A student in the year 1895 prepared three chromium compounds all of which corresponded to the same formula of $CrCl_3.6H_2O$. When each of the compounds is dissolved in water, the number of Cl^- ions released are as indicated below:

Complex: colour	Free Cl^- ions in solution per Formula Unit
A: Violet	3
B: Light green	2
C: Dark green	1

i) Write the formulas of these compounds

ii) Suggest a method (involving wet chemistry) for confirming the number of Cl^- ions in the outer coordination sphere per formula unit of each complex.

[11]

Question Four

a) For each of the following pairs of species, indicate which member of the pair is more acidic. Explain each of your answers.

i) VO_2 or CoO_2 ii) CrO_3 or WO_3 iii) FeO or Fe_2O_3

[6]

b) In order to separate gold from solid impurities, the ore is treated with a sodium cyanide (NaCN) solution in the presence of air to dissolve the gold by forming a soluble complex.

i) Write a balanced chemical equation that depicts the formation of the complex.

ii) Give the geometry of the complex

[6]

c) Predict the ***spin-only*** magnetic moment of each of the following octahedral complexes. In each case use a suitable CF (d-orbital) splitting diagram to illustrate how the spin quantum number (S) is obtained.

i) $[Fe(CN)_6]^{3-}$

iii) $[FeF_6]^{3-}$

[7]

d) Assume that the trans effect increases in the order NH_3 **<Cl^- < NO_2^- < PR_3.** Suggest the structures of the products arising from the reactions of $[PtCl_4]^{2-}$ with the ligands given below. In each case the structures of the products and sequences of reactions should be clearly shown.

i) Two equivalents of NH_3

ii) One equivalent of PEt_3 followed by one equivalent of NO_2^-.

[6]

Question Five

a) Consider formation constants for the following reactions (at 298K):

Reaction No.	Reaction Equation	Formation Constant
1.	$Ag^+ + 2NH_3 \rightleftarrows [Ag(NH_3)_2]^+$	K_1=1.5 x10^7
2.	$Ag^+ + 2CN^- \rightleftarrows [Ag(CN)_2]^-$	K_2=1.0 x 10^{21}
3.	$[Ag(NH_3)_2]^+ + 2CN^- \rightleftarrows [Ag(CN)_2]^- + 2NH_3$	K_3

i) Write the expressions for the equilibrium constant K_1, K_2 and K_3 in terms of concentrations of the appropriate species.

ii) Calculate the value for K_3

iii) Comment on the relative sizes of the equilibrium constants K_1 and K_2.

[5]

b) Overall stability constants for $[Au(CN)_2]^-$ and $[Pd(CN)_4]^{2-}$ are $\log\beta_2=39$ and $\log\beta_4=62.3$, respectively. Write reaction equations that describe the processes to which these constants refer. Then write the expressions to define β_2 and β_4 (in terms of concentrations of appropriate species).

[6]

c) Predict whether the equilibrium for the following reactions is expected to lie more on the right hand side or more on the left hand side. Explain each of your answers.

i) $CdI_2 + CaF_2 \rightleftarrows CdF_2 + CaI_2$

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

iii) $CH_3Hg^+ + HCN \rightleftarrows CH_3HgCN + H^+$

[6]

d) The extent of crystal field splitting is often determined from optical spectra.

i) Given the wavelength (λ) of maximum absorption, find the crystal field splitting energy (Δo), in kJ/mol, for each of the following complex ions:

COMPLEX ION	λ (nm) for Δ_o
$[Cr(H_2O)_6]^{3+}$	562
$[Cr(CN)_6]^{3-}$	381
$[CrCl_6]^{3-}$	735
$[Cr(NH_3)_6]^{3+}$	462
$[Ir(NH_3)_6]^{3+}$	244
$[Fe(H_2O)_6]^{2+}$	966
$[Fe(H_2O)_6]^{3+}$	730
$[Co(NH_3)_6]^{3+}$	405
$[Rh(NH_3)_6]^{3+}$	295

ii) Construct a spectrochemical series for the ligands in the Cr complexes

iii) Use the Fe data to state how oxidation state affects Δ_o

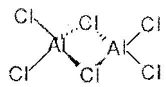
iv) Use the Co, Rh and Ir data to state how period number affects Δ_o.

[8]

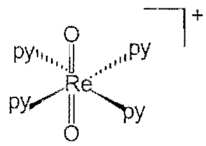
Question Six

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

i) Al_2Cl_6



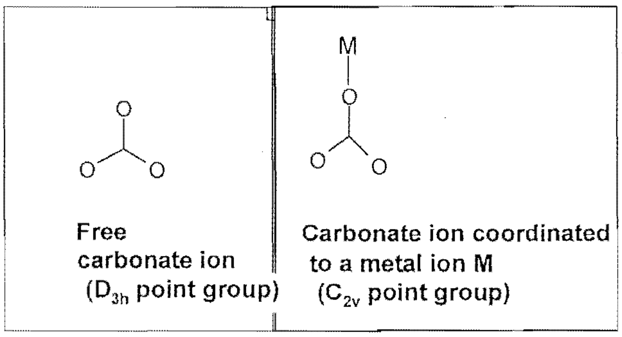
ii) *Trans*-$[Re(O)_2(py)_4]^+$



[6]

b) The carbonate ion, CO_3^{2-}, can serve as a ligand. When it does so, the symmetry is lowered from D_{3h} (for the uncoordinated ion), to C_{2v} (for the monodentate ligand or bidentate ligand). Thus infrared spectroscopy makes it possible to distinguish coordinated carbonate from uncoordinated carbonate. Using internal coordinates, $\mathbf{r}_i$, determine the symmetries and number of C-O stretching IR active and Raman active bands for

i) Uncoordinated carbonate
ii) Monodentate carbonate, $M\text{-}O\text{-}CO_2$, where M= metal center



[19]

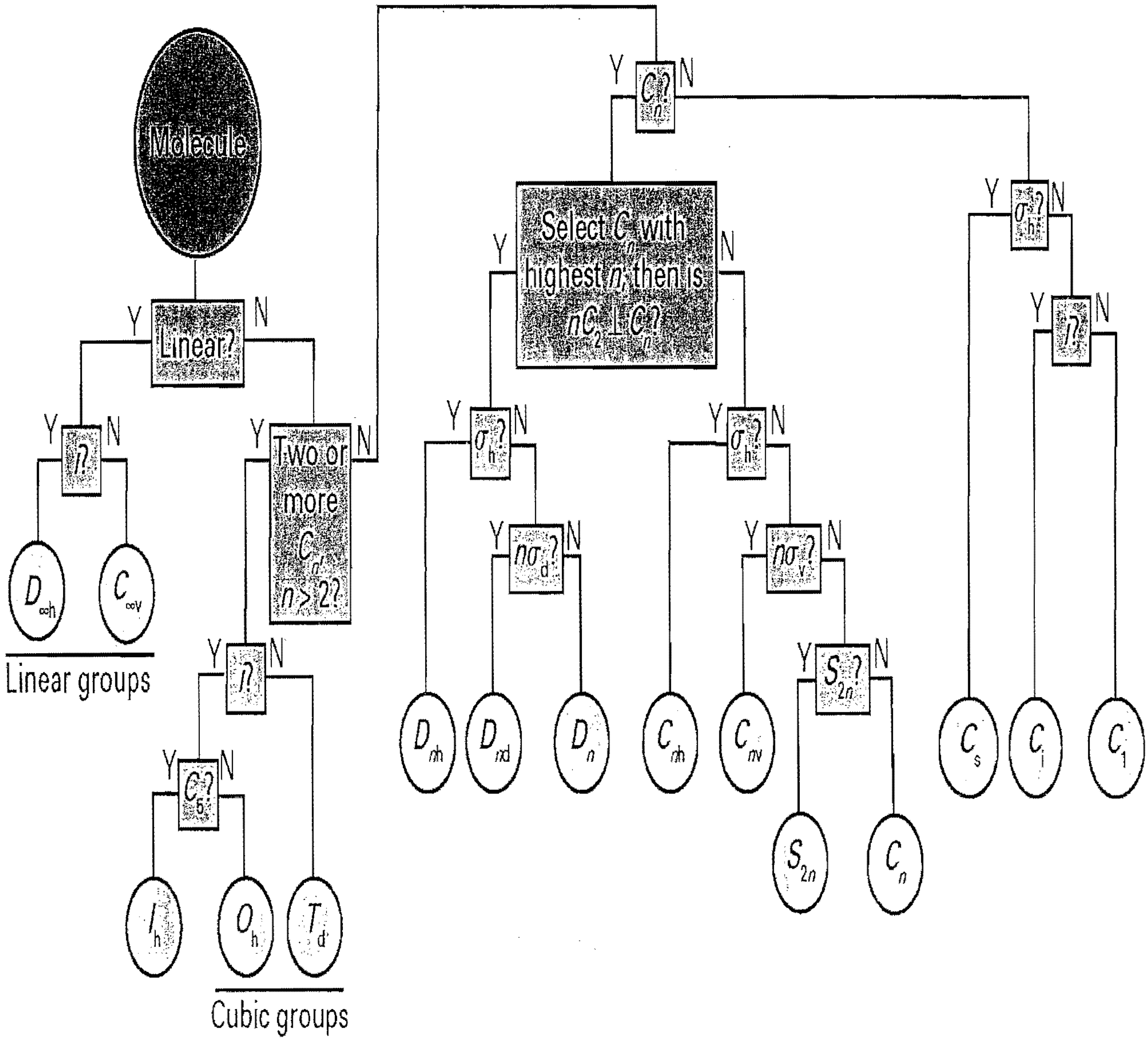
C301

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

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

D_{3h} ($\bar{6}m2$)	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	$h=12$	
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(zx, yz)

CHE321/C301 Decision Tree (Flow Chart)



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

CHE 322/C301

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.

C301 /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