

UNIVERSITY OF SWAZILAND
SUPPLEMENTARY FINAL EXAMINATIONS
ACADEMIC YEAR 2009/2010

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
- ❖ Tanabe-Sugano diagrams for d^2 , d^3 , d^4 and d^5 octahedral complexes
- ❖ Character tables for C_{2v} and D_{3h} point groups
- ❖ Decision Tree

ELECTRONIC CALCULATORS MAY BE USED

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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) $\text{K}_5[\text{Mo}(\text{CN})_7]$
- ii) $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$
- iii) $[\text{Co}(\text{OH}_2)_6](\text{ClO}_4)_2$
- iv) $\text{K}_2[\text{NiCl}_4]$

[6 mks]

b) Give the formula of each of the following:

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

[6 mks]

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

- i) $[\text{Rh}(\text{Cl})_2(\text{en})_2]^+$
- ii) $[\text{RuCl}_5(\text{SCN})]^{4-}$
- iii) $\text{Ru}(\text{NH}_3)_3\text{Br}_3$

[13 mks]

Question Two

i) Sketch the structures of all possible isomers that may arise from the following complexes:

- i) $[\text{Ni}(\text{SCH}_2\text{CH}_2\text{NH}_2)_2]$, square planar
- ii) $[\text{Co}(\text{en})_3]^{3+}$

[6 mks]

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

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

[4 mks]

- c) Stepwise stability constants (at 303K) of $[[Ni(OH_2)_{6-x}(NH_3)_x]]$, where $x=1-6$, have been found to be as follows:

$$\log K_1 = 2.79$$

$$\log K_2 = 2.26$$

$$\log K_3 = 1.69$$

$$\log K_4 = 1.25$$

$$\log K_5 = 0.74$$

$$\log K_6 = 0.03$$

- i) Give the reaction equation that corresponds to each of the equilibria
- ii) Give the expressions for K_6 and β_6 (in terms of concentrations)
- iii) Calculate the value of β_6
- iv) Calculate ΔG° at 303K corresponding to β_6
- v) Supposing ethylenediamine is used in place of NH_3 , do you expect β_6 to be smaller or larger? Explain your answer.

[15 mks]

Question Three

- a) Write down the **formula** for each of the following:

- i) Sodium trichloroammineplatinate (II)
- ii) *mer*-Trichlorotris(triphenylphosphine)ruthenium(III)
- iii) Potassium pentacyanonitrosylferrate(II) dihydrate

[6 mks]

- b) The value of the molar extinction coefficient, ϵ_{max} , for the most intense band in the electronic spectrum of $[CoCl_4]^{2-}$ differs from that of $[Co(OH_2)_6]^{2+}$ by a factor of 100. Comment on this observation and state which complex is expected to exhibit a higher value of ϵ_{max} .

[7 mks]

- c) The electronic spectrum of a solution containing $[V(OH_2)_6]^{3+}$ exhibits two bands which are found around 17200 and 25600 cm^{-1} . Assign the bands and state whether the number of bands observed is consistent with the Tanabe-Sugano diagram for the complex. If any band is missing, suggest an explanation.

[6 mks]

- d) Red crystalline $[NiCl_2(Ph_2PCH_2CH_2PPh_2)]$ is diamagnetic. On heating to 387K for two hours, a blue-green form of the complex is obtained which has a magnetic moment of 3.18 BM at 295 K. Suggest an explanation for the observations and draw the structures for the complexes.

[6 mks]

Question Four

- a) Consider the ligands CO, F⁻, and NH₃, and then answer the following questions:
- Classify the ligands as being σ -donor only, σ -donor plus π -donor or σ -donor plus π -acceptor
 - State which orbitals are involved in π -bond formation, if any, with the metal ion in an octahedral complex. Give diagrams to illustrate how the overlap takes place
- [6 mks]**
- b) Obtain ground state terms of free ions with the following electron configurations:
- 3d²
 - 3d⁸
- [4 mks]**
- c) What is the "hole formalism"? Give two examples to illustrate your answer.
- [4 mks]**
- d) State the following rules:
- The spin selection rule
 - The Laporte selection rule
- [3 mks]**
- f) Explain the origins of LMCT and MLCT absorptions in the electronic spectra of d-block metal complexes. Give two examples (one for each type) to illustrate your answer.
- [8 mks]**

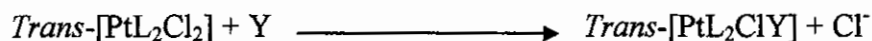
Question Five

- a) Briefly discuss the observed trends in the stability of oxidation states across the periods from left to right and down the groups. Use examples to illustrate your answer.
- [6 mks]**
- b) The value of the magnetic moment, μ_{eff} for [CoF₆]³⁻ is found to be 5.63 BM. Explain why this value does not agree with the value for magnetic moment calculated using the spin-only formula.
- [5 mks]**

- c) Give the products that are formed and rationalize the nature of products formed when $[\text{PtCl}_4]^{2-}$ reacts with NH_3 and NO_2^- as follows:
- $[\text{PtCl}_4]^{2-}$ first reacts with one equivalent of NH_3 to form a product (P_1) which then reacts with one equivalent of NO_2^- to form the final product (P_2)
 - $[\text{PtCl}_4]^{2-}$ first reacts with one equivalent of NO_2^- to form a product (P_3) which then reacts with one equivalent of NH_3 to form the final product (P_4)

[6 mks]

- ii) Suggest a mechanism for the following stereoselective reaction:



[4 mks]

- iii) Rationalize why $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{2-}$, both octahedral Fe(II) complexes, are paramagnetic and diamagnetic respectively.

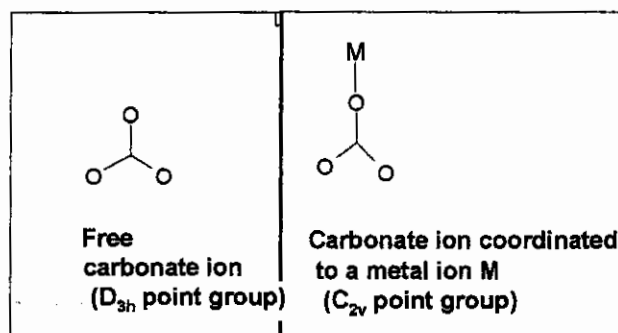
[4 mks]

Question Six

- a) 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, determine the symmetries and number of stretching IR active and Raman active bands for

- Uncoordinated carbonate
- Monodentate carbonate, M-O-CO_2 , where M= metal center

[20 mks]



- b) Two isomeric six-coordinate coordination compounds have the formula $\text{Co}(\text{NH}_3)_5\text{Br}(\text{SO}_4)$. Give the formulas of the two complexes. What chemical tests would you carry out to distinguish the two isomers?

[5 mks]

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	VIIA	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														18.998 F 9	17.004 O 8	20.180 Ne 10	
3	22.990 Na 11	24.305 Mg 12														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

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
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

* Lanthanide series

** Actinide series

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 ¹²C = 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.

PHYSICAL AND CHEMICAL CONSTANTS

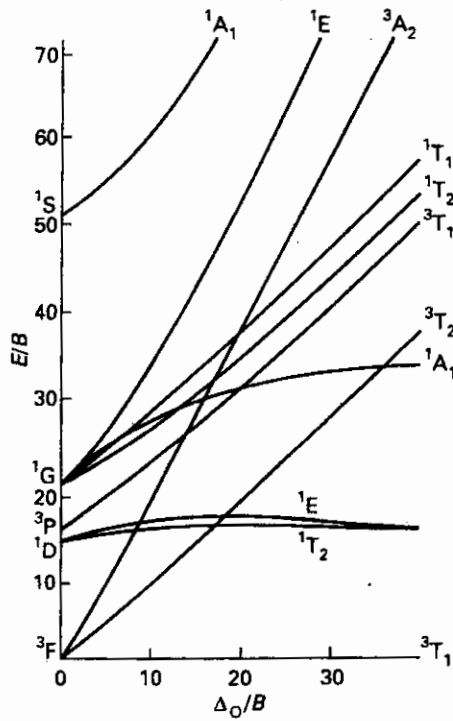
Avogadro's number	$N_A = 6.022045 \times 10^{23} \text{ mol}^{-1}$
Electron charge	$e = 4.8030 \times 10^{-10} \text{ abs esu}$ $= 1.6021892 \times 10^{-19} \text{ C}$
Electron mass	$m_e = 9.1091 \times 10^{-31} \text{ kg}$ $= 5.4860 \times 10^{-4} \text{ amu}$ $= 0.5110 \text{ MeV}$
Proton mass	$m_p = 1.6726485 \times 10^{-27} \text{ kg}$ $= 1.007276470 \text{ amu}$
Gas constant	$R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$ $= 1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$ $= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$
Ice point	$= 273.15 \text{ K}$
Molar volume	$= 22.414 \times 10^3 \text{ cm}^3 \text{ mol}^{-1}$ $= 2.2414 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$
Planck's constant	$h = 6.626176 \times 10^{-34} \text{ J s}$ $= 6.626176 \times 10^{-27} \text{ erg s}$
Boltzmann's constant	$k = 1.380662 \times 10^{-23} \text{ J K}^{-1}$
Rydberg constant	$\mathcal{R} = 1.097373177 \times 10^{-7} \text{ m}^{-1}$
Faraday's constant	$\mathcal{F} = 9.648670 \times 10^4 \text{ C mol}^{-1}$
Speed of light	$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$
Bohr radius	$a_0 = 0.52917706 \times 10^{-10} \text{ m}$
Other numbers	$\pi = 3.14159$ $e = 2.7183$ $\ln 10 = 2.3026$

CONVERSION FACTORS

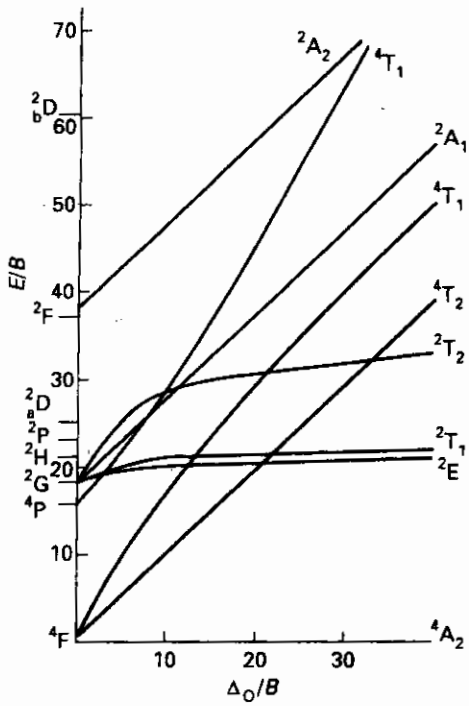
1 cal	$= 4.184 \text{ joules (J)}$
1 eV/molecule	$= 96.485 \text{ kJ mol}^{-1}$ $= 23.061 \text{ kcal mol}^{-1}$
1 kcal mol ⁻¹	$= 349.76 \text{ cm}^{-1}$ $= 0.0433 \text{ eV}$
1 kJ mol ⁻¹	$= 83.54 \text{ cm}^{-1}$
1 wave number (cm ⁻¹)	$= 2.8591 \times 10^{-3} \text{ kcal mol}^{-1}$
1 erg	$= 2.390 \times 10^{-11} \text{ kcal}$
1 centimeter (cm)	$= 10^8 \text{ \AA}$ $= 10^7 \text{ nm}$
1 picometer (pm)	$= 10^{-2} \text{ \AA}$
1 nanometer (nm)	$= 10 \text{ \AA}$

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

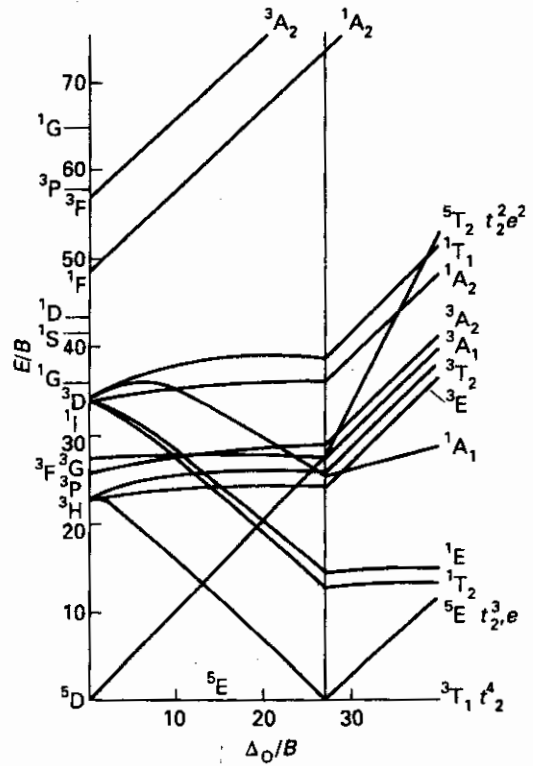
d^2



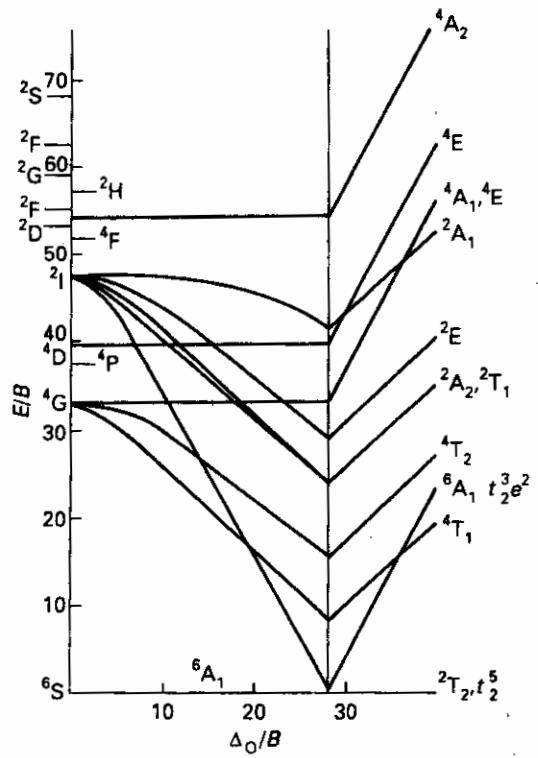
2. d^3 with $C = 4.5B$



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



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



CHARACTER TABLES.

C_{2v}

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	$h = 4$
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, zx
B_2	1	-1	-1	1	y, R_x, yz

D_{3h}

D_{3h}	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	$(R_x, R_y), (zx, yz)$

C301
Point
Group
Flow Chart

