UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2013

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 formula for the following complexes:

(i) Carbonatopentaamminecobalt(III) chloride

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

iii) Potassium tetrabromocuprate(II)

[9]

c) What is meant by tetragonal and trigonal distortion of an octahedron? Illustrate your answer with a drawing for each case.

[10]

Question Two

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

(i) *mer*- bis(acetonitrile)trichloridooxoniobium(V)

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

[5]

b) Determine the oxidation state and number of d electrons for the metal centre 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 formula of 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) both oxygen and nitrogen

[6]

d) Describe how pi-donor and pi-acceptor ligands can control the preferred oxidation states of transition metal ions. Give one example for each type of ligands.

[8]

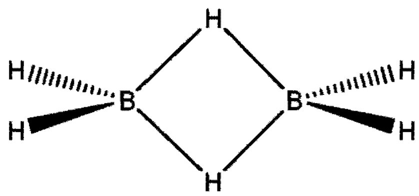
Question Four

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

[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.

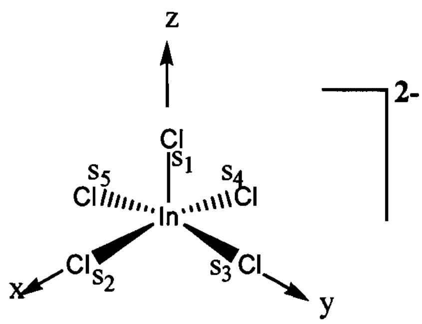
i) Draw structures the two possible isomers

ii) Work out the symmetry-allowed IR and Raman v(Pd-Cl) bands for the ***trans*** isomer **only**. [Let the z axis be perpendicular to the plane of the molecule and then let x and y axes coincide with Cl-Pd-Cl and CO-Pd-CO axes respectively].

[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 s (sigma-type) orbitals.



a) Given that the point group of the complex is C_{4v}, generate a reducible representation of the ligand s orbitals and decompose it into irreducible representations.

[5]

b) Use the projection operator method to generate SALCs for the irreducible representations obtained in a) above for the ligand s orbitals.

[8]

c) From the results obtained in a) and b) above, create a table with column headings as shown below. For each irreducible representation, Γ_s, of the ligand s orbitals, list matching atomic orbital(s) on In. Also enter in the table corresponding SALCs. **[6]**

Irreducible representation, Γ_s, from ligand s orbitals,	Valence atomic orbital(s) on central atom, In	SALCs of ligand s orbitals corresponding to Γ_s

d) Using the data in c) above, give four possible hybridization schemes for bonding between ligand s 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 a 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 a complex with the following Lewis bases. Explain your answer.

i) BH_3 ii) BF_3

[4]

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

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

[9]

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.

PHYSICAL AND CHEMICAL CONSTANTS

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

CONVERSION FACTORS

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

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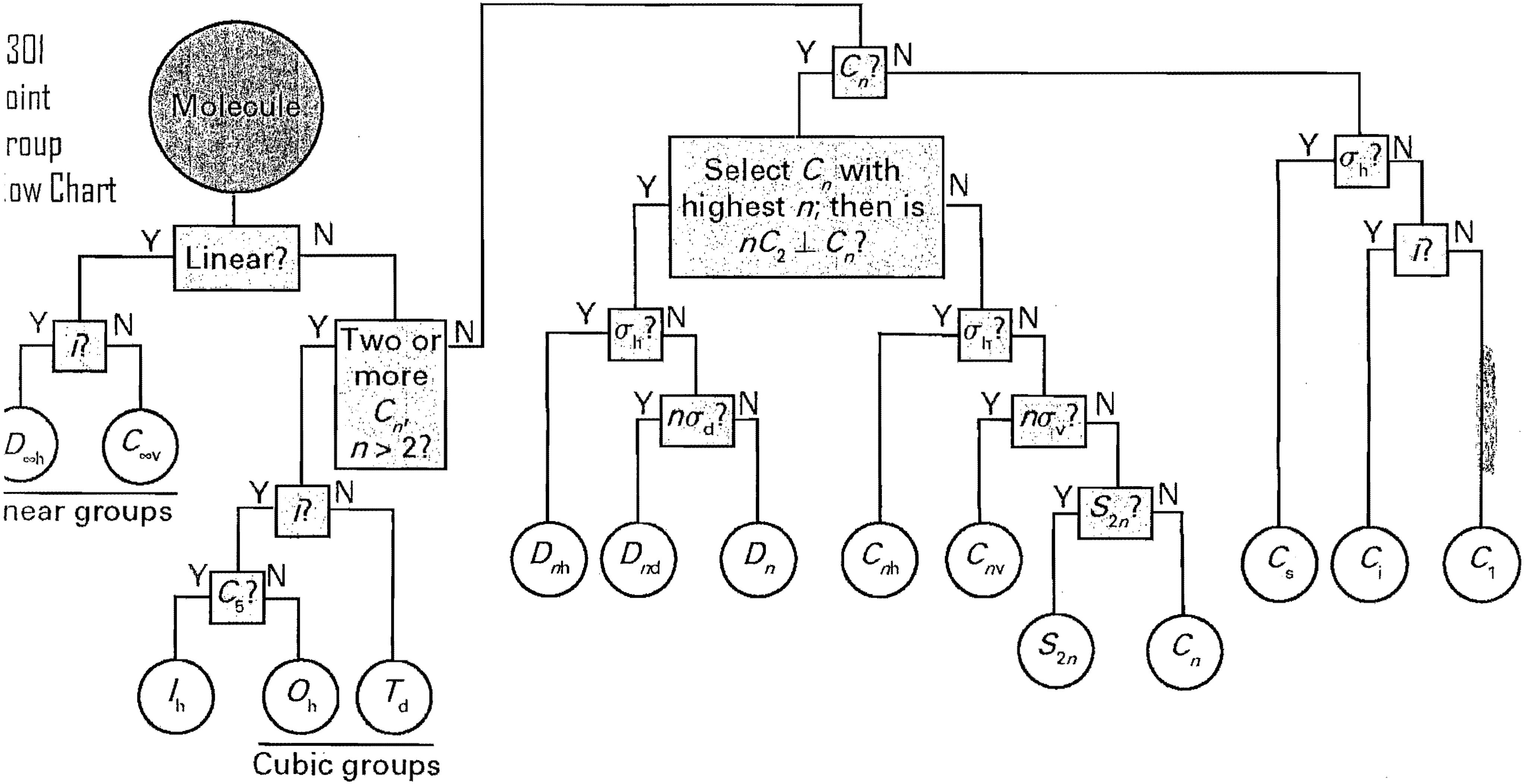


CHARACTER TABLES

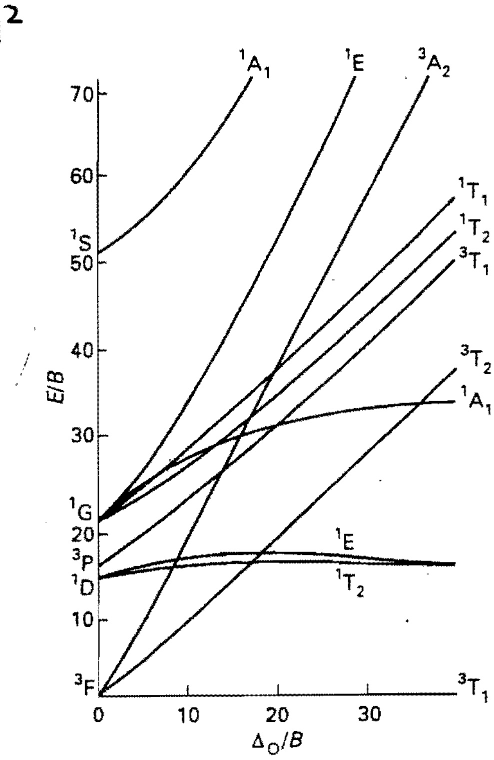
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y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

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	

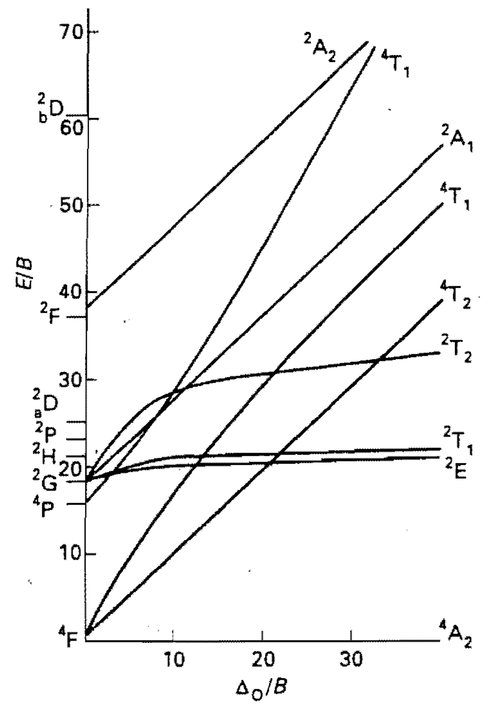
C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

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

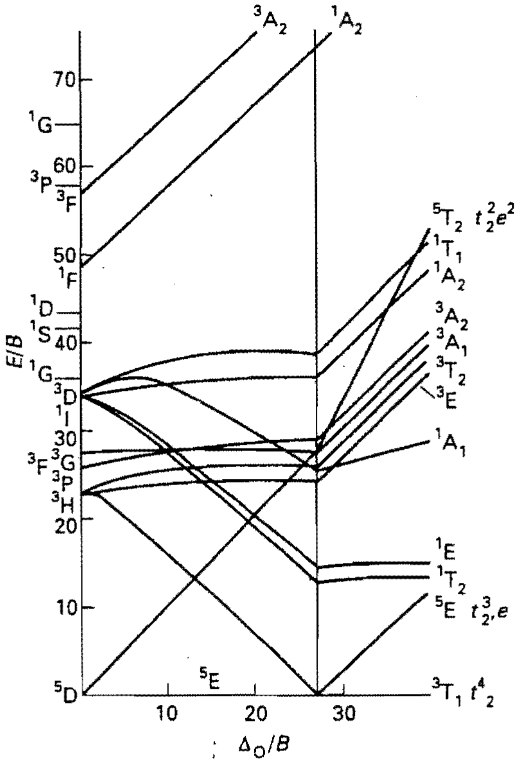
d^2



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



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



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