UNIVERSITY OF SWAZILAND

SUPPLEMENTARY FINAL EXAMINATION

ACADEMIC YEAR 2011/2012

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.

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Question One

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

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

[8]

b) Give the formula of each of the following:

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

[6]

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

i) $[Pt(en)_2Cl_2]^{2+}$
ii) $Pd(bpy)(NCS)_2$

[11]

Question Two

a) Using hard-soft concepts, which of the following reactions are predicted to have an equilibrium constant greater than 1? Briefly explain each of your answers.

i) $ZnO + 2BuLi \rightleftharpoons Zn(Bu)_2 + Li_2O$

ii) $R_3PBBr_3 + R_3NBF_3 \rightleftharpoons R_3PBF_3 + R_3NBBr_3$

iii) $CH_3HgI + HCl \rightleftharpoons CH_3HgCl + HI$

iv) $[AgCl_2]^- + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^- + 2Cl^-$

[8]

b) The value of μ_{eff} for $[CoF_6]^{3-}$ is found to be 5.63 BM. Given that the complex contains a d^6 Co(III) metal center, 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. With respect to what are orbital energies raised or lowered? **[7]**

d) What is the expected ordering of Δ_o for $[Fe(OH_2)_6]^{2+}$, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$? Rationalize your answer. **[4]**

Question Three

a) Using only ethylenediamine (en = $H_2NCH_2CH_2NH_2$) and bromide ions as ligands, construct a cationic octahedral complex of cobalt(III). Your complex cation should have +1 charge and it should be chiral. Draw a three-dimensional structure for this complex together with its mirror image. Then draw the structure of the diastereoisomer of the enantiomers you have drawn.

[9]

b) Consider the salt $[Co(bpy)_2(CN)_2]^+[Fe(bpy)(CN)_4]^-$.

i) Give formulas for compounds that are coordination isomers of the salt

ii) Draw two geometrical isomers arising from **only one** of the ions

iii) Draw two enantiomers arising from **only one** of the ions

[16]

Question Four

a) Consider a substitution reaction involving a coordination complex ML_5X and an entering group Y:

$$ML_5X + Y \rightleftarrows ML_5Y + X$$

The limiting mechanisms are the dissociative mechanism (D) and the associative mechanism (A). For each of the two limiting mechanisms, sketch a labelled diagram depicting the reaction profile. In each case, the labelled parts should include activation energy, intermediate(s) and activated complex(es).

[9]

b) For a substitution reaction shown below, the rate of reaction is found to be first order in each of the two starting materials. Suggest a mechanism for the reaction.

$$Co(NO)(CO)_3 + As(C_6H_5)_3 \rightleftarrows Co(NO)(CO)_2(As(C_6H_5)_3) + CO$$

[4]

c) Using the concept of the *trans-effect*, predict the products (including structures) of the following reactions:

i) $PtCl_4^{2-} + NO_2^- \rightarrow A$
$A + NH_3 \rightarrow B$

ii) $[PtCl_3(NH_3)]^- \rightarrow C$
$C + NO_2^- \rightarrow D$

iii) $[PtCl_4]^- + NH_3 \rightarrow E$
$E + NH_3 \rightarrow F$

[12]

Question Five

a) Consider adding an aqueous solution of ammonia to an aqueous solution of copper(II) sulphate. Initially, a pale blue precipitate is formed. Upon adding excess ammonia solution, the precipitate dissolves resulting in the formation of a deep blue solution. Use suitable equations to explain the above observations.

[5]

b) The electronic spectrum $[Co(H_2O)_6]^{2+}$ exhibits bands at 8100, 16000 and 19400 cm^{-1}.

i) Assuming the complex has a high-spin electronic ground state, assign electronic transitions to these bands (listed above)

ii) Consider a cobalt(II) complex $[Co(CN)_6]^{4-}$. Comment on the nature of the ground state and the spin-allowed transitions expected

[14]

d) Complete and balance the following reactions:

i) $Cr + Cl_2 \longrightarrow$

ii) $Mo + Cl_2 \longrightarrow$

iii) $Cr + O_2 \longrightarrow$

iv) $Mo + O_2 \longrightarrow$

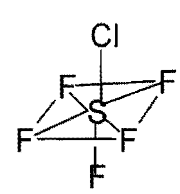
[6]

Question Six

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

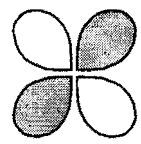
i) Cis-$[PtCl_2BrI]^{2-}$

ii) SF_5Cl



iii) *trans*-$Co(Br)(Cl)(NH_3)_4$

iv) d_{xy} orbital (whose shape is sketched below)



[12]

b) Determine the symmetries of M-Cl **stretching modes** for the six-coordinate complex [$MCl_5(O)$] (which has C_{4v} point group). Which of the modes are IR active? Which ones are Raman active?

[13]

The Periodic Table

Period	1	2	3	4	5	6	7	8	9	10	11	12	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	La-Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210.0	85 At 210.0	86 Rn 222.0
7	87 Fr 223.0	88 Ra 226.0	Ac-Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	......								
	s block		*d* block										*p* block					

	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Lanthanides	La 138.9	Ce 140.1	Pr 140.9	Nd 146.2	Pm 144.9	Sm 150.4	Eu 152.0	Gd 157.2	Tb 158.9	Dy 162.5	Ho 164.9	Er 167.3	Tm 168.9	Yb 173.0	Lu 175.0
	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Actinides	Ac 227.0	Th 232.0	Pa 231.0	U 238.0	Np 237.0	Pu 239.1	Am 241.1	Cm 244.1	Bk 249.1	Cf 252.1	Es 252.1	Fm 257.1	Md 258.1	No 259.1	Lr 262.1
	f block														

Useful relations

At 298.15 K, $RT = 2.4790$ kJ mol^{-1} and $RT/F = 25.693$ mV

1 atm = 101.325 kPa = 760 Torr (exactly)

1 bar = 10^5 Pa

1 eV = $1.602\ 18 \times 10^{-19}$ J = 96.485 kJ mol^{-1} = 8065.5 cm^{-1}

1 cm^{-1} = 1.986×10^{-23} J = 11.96 J mol^{-1} = 0.1240 meV

1 cal = 4.184 J (exactly)

1 D (debye) = $3.335\ 64 \times 10^{-30}$ C m

1 T = 10^4 G

1 Å (ångström) = 100 pm

1 M = 1 mol dm^{-3}

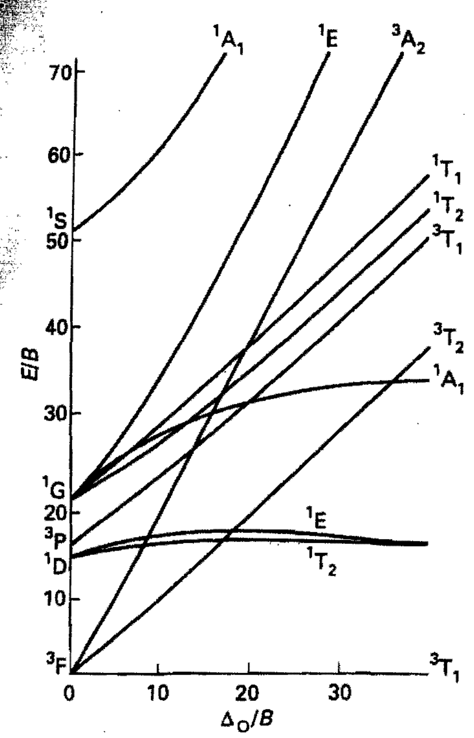
General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\ 925 \times 10^8$ m s^{-1}
Elementary charge	e	$1.602\ 177 \times 10^{-19}$ C
Faraday constant	$F = eN_A$	9.6485×10^4 C mol^{-1}
Boltzmann constant	k	$1.380\ 66 \times 10^{-23}$ J K^{-1}
		8.6174×10^{-5} eV K^{-1}
Gas constant	$R = kN_A$	$8.314\ 51$ J K^{-1} mol^{-1}
		$8.205\ 78 \times 10^{-2}$ dm^3 atm K^{-1} mol^{-1}
Planck constant	h	$6.626\ 08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\ 57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\ 14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\ 54 \times 10^{-27}$ kg
Mass of electron	m_e	$9.109\ 39 \times 10^{-31}$ kg
Vacuum permittivity	ε_0	$8.854\ 19 \times 10^{-12}$ J^{-1} C^2 m^{-1}
	$4\pi\varepsilon_0$	$1.112\ 65 \times 10^{-10}$ J^{-1} C^2 m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\ 02 \times 10^{-24}$ J T^{-1}
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\ 77 \times 10^{-11}$ m
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^2$	$1.097\ 37 \times 10^5$ cm^{-1} $= 1.09737 \times 10^7$ m^{-1}

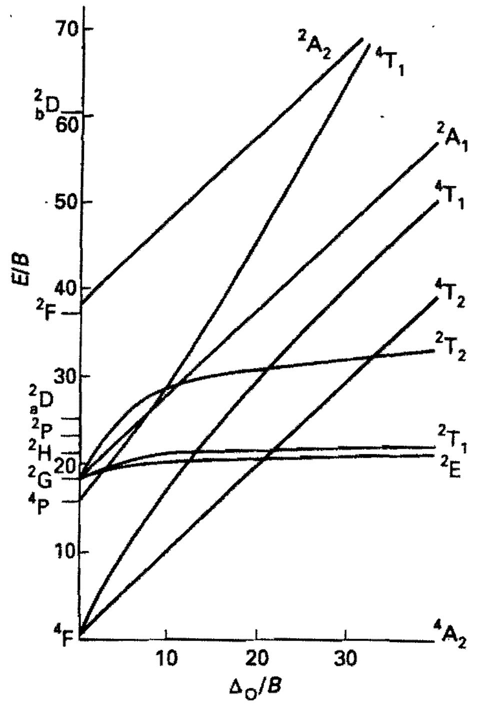
Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^3	10^6	10^9

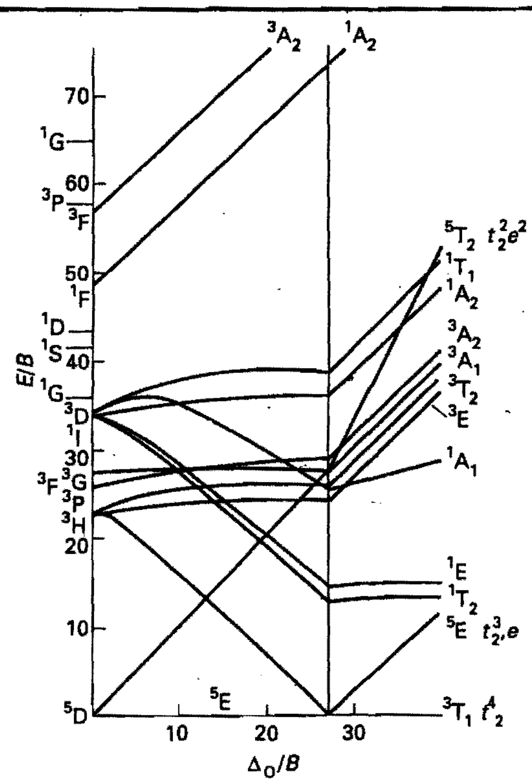
1. d^2 with $C = 4.42B$



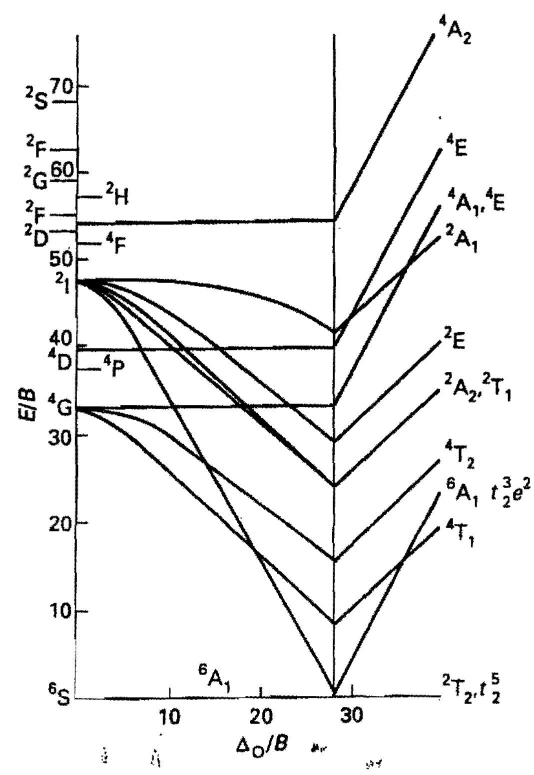
2. d^3 with $C = 4.5B$



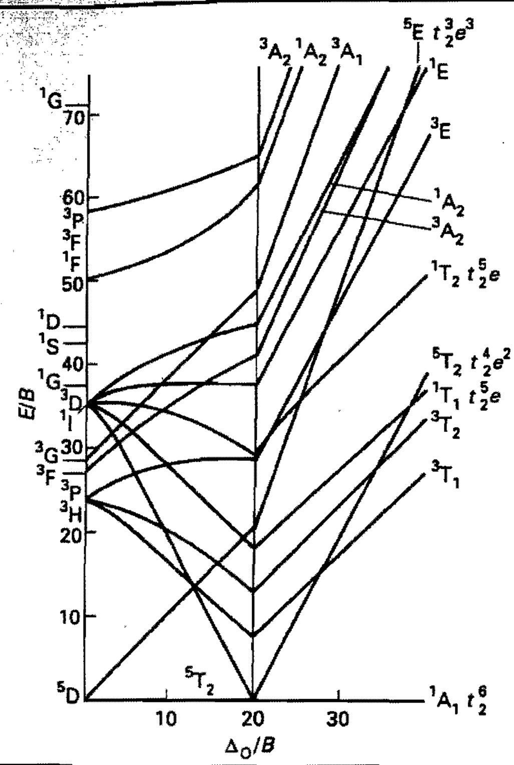
3. d^4 with $C = 4.61B$



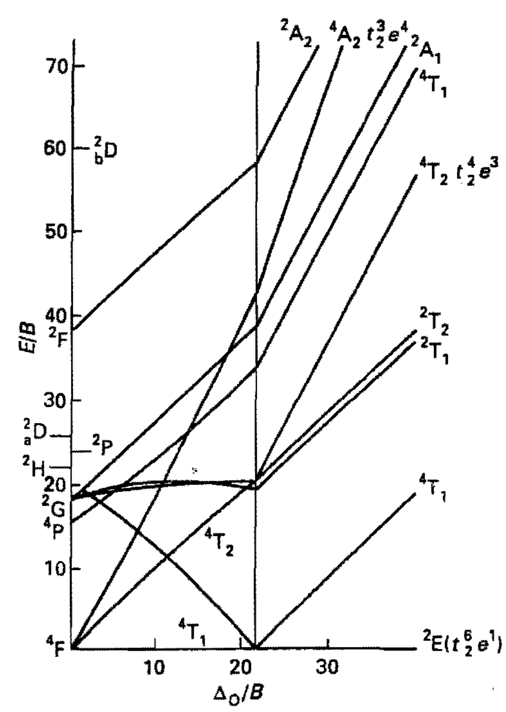
4. d^5 with $C = 4.477B$



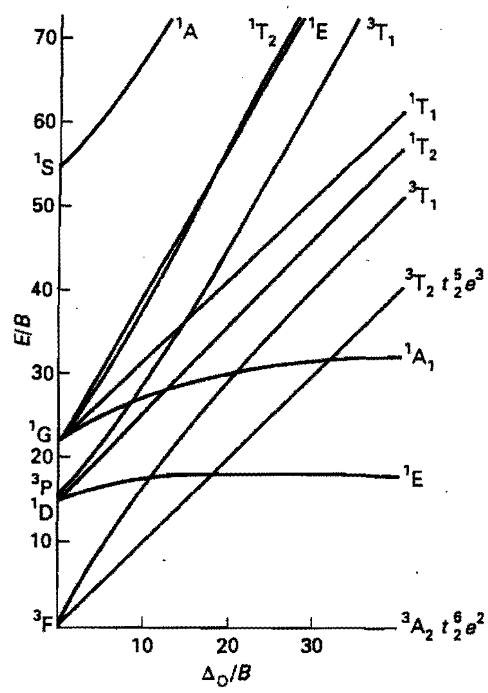
5. d^6 with $C = 4.8B$

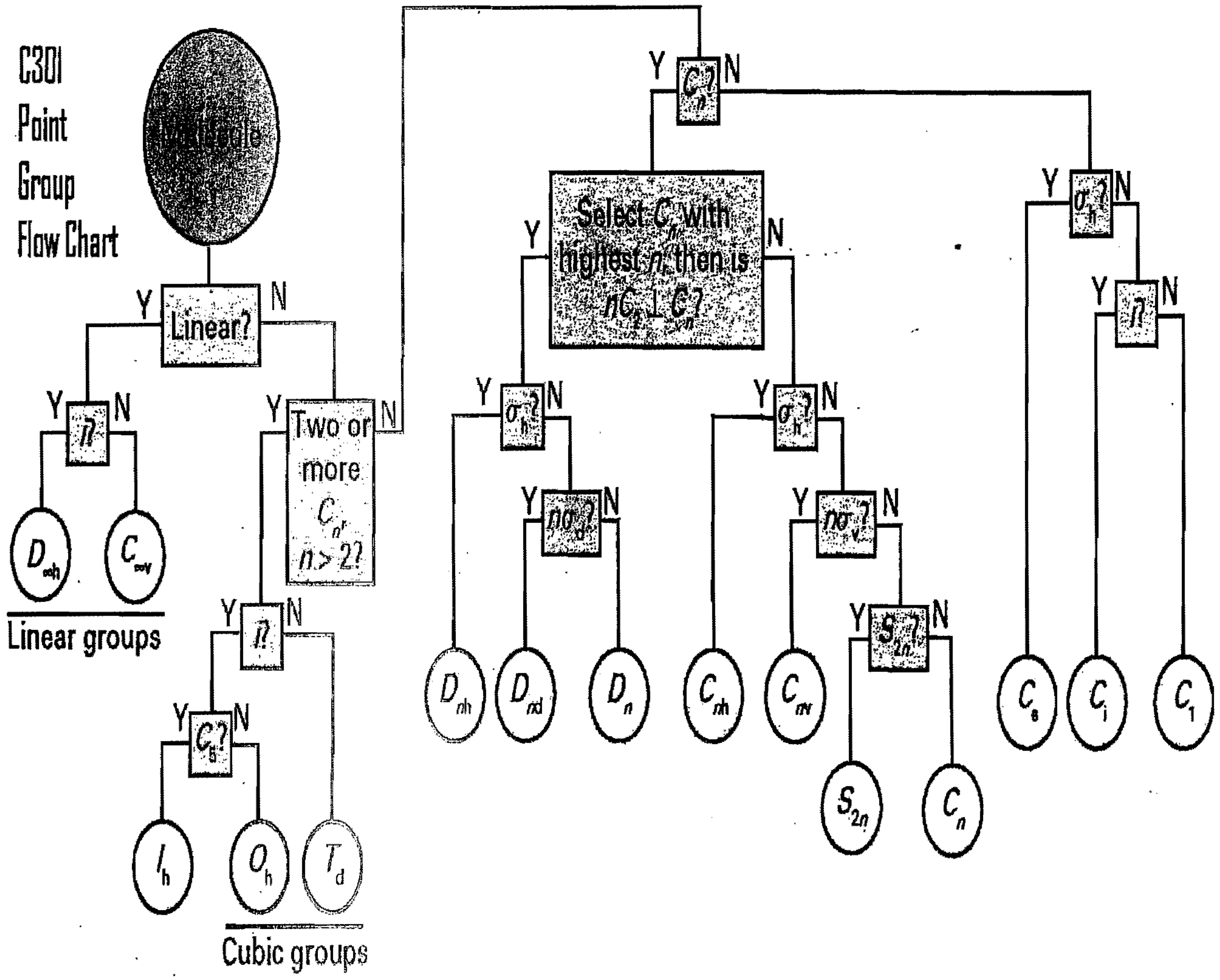


6. d^7 with $C = 4.633B$



7. d^8 with $C = 4.709B$




C301
Point
Group
Flow Chart
Molecule
Linear?
Y
N
n
$D_{\infty h}$
$C_{\infty v}$
Linear groups
Two or more C_n, $n > 2$?
n
C_5?
I_h
O_h
T_d
Cubic groups
C_n?
Select C_n with highest n, then is $nC_2 \perp C_n$?
σ_h?
$n\sigma_d$?
D_{nh}
D_{nd}
D_n
$n\sigma_v$?
S_{2n}?
C_{nh}
C_{nv}
S_{2n}
C_n
C_s
C_i
C_1

C301: CHARACTER TABLES

4. The C_{nv} 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_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_x	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

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)

6. The D_{nh} Groups

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	

* 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_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		$x^2 - y^2$
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	