UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2010/2011

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. THERE ARE SEVEN (7) PAGES.

A PERIODIC TABLE AND A TABLE OF CONSTANTS HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

ELECTRONIC CALCULATORS MAY BE USED

PLEASE DO NOT OPEN THIS PAPER UNTIL AUTHORISED TO DO SO BY THE CHIEF INVIGILATOR.

"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) $Li[AlH_4]$
ii) $[Pt(py)_4][PtCl_4]$
iii) $Na_3[Ag(S_2O_3)_2]$, $S_2O_3^{2-}$ = thiosulphate ion
iv) $[(H_3N)_5Cr\text{-}OH\text{-}Cr(NH_3)_5]Cl_5$

[6 mks]

b) Give the formula of each of the following:

i) Tetraoxomanganate(VII)
ii) Bis(acetyacetonato)oxovanadium(IV)
iii) Potassium amminedicyanodioxoperoxochromate(VI)
iv) Potassium pentachloronitridoosmate(VI)

[6 mks]

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

i) $Mo(CO)_4(MeCN)_2$

ii) $[Cu(NH_3)_4][PtCl_4]$

iii) $[Co(SCH_2CH_2NH_2)_3]$

[13 mks]

Question Two

a) For the ions Cu^{2+} and Ti^{3+}, identify the ground state terms (with the spin multiplicity) for the following cases:

i) Free ions

ii) Octahedral complexes

iii) Tetrahedral complexes

[7]

b) Negatively charged ions are expected to create stronger ligand fields than neutral molecules. Explain the following:

i) The hydroxide ion, OH^-, is a weaker field ligand than H_2O

ii) CO is such a strong field ligand

[10]

a) Give equations to show the reactions between CrO, Cr_2O_3 and CrO_3 with

i) aqueous acids

ii) aqueous bases

[8]

Question Three

a) Consider the following data for the complex $[Ni(NH_3)_6]^{2+}$:

$[Ni(NH_3)_6]^{2+}$	**Molar absorptivity**
10700 cm^{-1}	5-10
17500	5-10
28300	5-10
15400	< 1
18400	<1

Assuming O_h symmetry, use the Tanabe-Sugano diagram provided to assign the bands. Explain your answer.

[5]

b) Use your knowledge of features of d-d and charge transfer spectra of octahedral complexes to match each lettered set of spectral data with the correct complex. Explain your answer.

Complex	**λ_{max} (in kK, 1kK=1000 cm^{-1})** **Note: weak means ε=5-100, strong means ε>10 000**
A	22.4(weak) 25.9(weak) 36.8(strong) 41.7(strong)
B	18.1(weak) 22.2(weak) 30.1 (strong) 33.9(strong)
C	23.9(weak) 30.1(weak)
D	32.7(weak) 39.1(weak)
E	19.3(weak) 24.3(weak) 39.2(strong)
F	16.6(weak) 24.9(weak)
Complexes: $[IrBr_6]^{3-}$, $[Co(H_2O)_6]^{3+}$, $[RhBr_6]^{3-}$, $[Rh(NH_3)_6]^{3+}$, $[RhCl_6]^{3-}$, $[Rh(H_2O)_6]^{3+}$	

[12]

c) Consider the complexes $[CoF_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. For each of these complexes,

i) Determine oxidation state and electron configuration for the metal ion

ii) Calculate the spin-only value of the magnetic moment

iii) Calculate the LFSE

iv) Determine whether the orbital contribution to the magnetic moment will be significant

[8]

Question Four

a) For each of the following complexes, draw one possible shape and name the shape you have drawn:

i) $[NiX_4]^{2-}$, X= anionic monodentate ligand

ii) $CrO(CF_3COCHCOCF_3)_2$

iii) $Fe(NO_3)_4$, Coordination No.=8

[8]

b) How might one distinguish between the following isomers?

i) $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$

ii) $[Co(H_2O)_6]Cl_3$ and $[Co(H_2O)_4(Cl)_2]Cl.2H_2O$

[8]

c) What is the number of d electrons for metal species usually encountered with the following stereochemistries? Give two examples of each type.

i) Linear

ii) Square planar

[6]

d) Consider intensities of absorption bands for isomers of a transition metal complex. Two isomers of a Co(III) complex, believed to be cis- and trans-isomers A and B, give the following spectral features. Each of them gives two absorption bands in the visible region. The two bands of isomer A are symmetrical and poorly resolved with ε=60-80. Those of isomer B are of lower intensity and well resolved. Assign the isomers and explain

[3]

Question Five

a) Give conditions and reactions involved during the extraction of gold from its ores. **[6]**

b) Compare and contrast the chemistry of the elements copper, silver and gold by considering the stability of their compounds with halides **[5]**

c) Base hydrolysis of the complex $[Co(NH_3)_5Cl]^{2+}$ obeys the rate law

Rate $=k[Co(NH_3)_5Cl^{2+}][OH^-]$

Give a reasonable mechanism for the hydrolysis of the complex and show that the mechanism you have proposed is consistent with the rate law given above **[8]**

d) To each of the redox reactions described below, assign an outer-sphere or inner-sphere electron-transfer mechanism. Explain your answer.

i) The main product of the reaction between $[Cr(OH_2)_4(NCS)F]^{2+}(aq)$ and $[Cr(H_2O)_6]^{2+}(aq)$ is $[Cr(H_2O)_5F]^{2+}(aq)$.

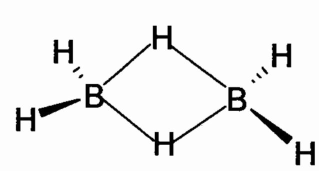
ii) When $[VO(edta)]^{2-}$ reacts with $[V(edta)]^{2-}$, a transient red colour is observed

iii) The rates of reduction of of $[Co(NH_3)_5py]$, where py represents pyridine, by $[Fe(CN)_6]^{4-}$ are not sensitive to substitution on py. That is, use of py, nitropyridine or methyl pyridine gives essentially the same rate constant. **[6]**

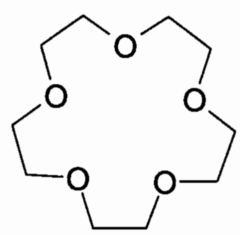
Question Six

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

i) B_2H_6

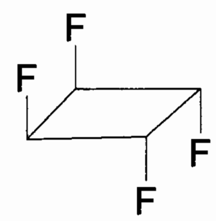


ii) 15-Crown-5



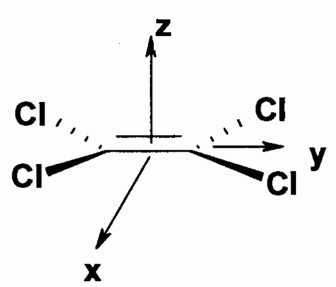
iii) F-N=N-F (cis)

iv) 1,2,3,4-Tetrafluorocyclobutane



[12]

b) Consider C-Cl stretching modes of vibration of a tetrachloroethylene molecule, $Cl_2C{=}CCl_2$, which has D_{2h} symmetry. Using the coordinate system given below where the xy-plane coincides with the plane of the molecule, answer questions that follow.



i) Determine symmetries of all the C-Cl stretching modes of vibration for the molecule

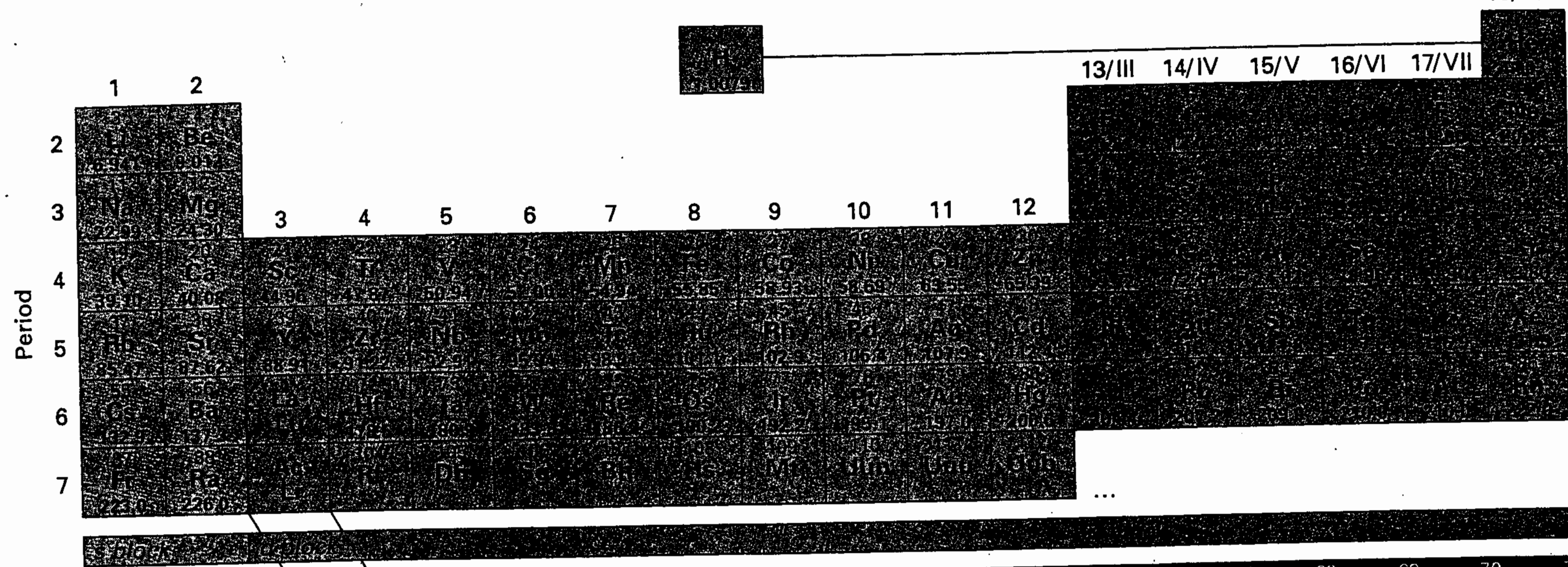
ii) Determine which of the species are IR active and which ones are Ra active

iii) Find the SALC's of the stretching modes of vibration from above

iv) Use the information in iii) above to sketch the stretching modes of vibration

[13]

The Periodic Table



Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
Actinides	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 239.1	95 Am 241.1	96 Cm 244.1	97 Bk 249.1	98 Cf 252.1	99 Es 252.1	100 Fm 257.1	101 Md 256.1	102 No 259.1	103 Lr 260.1

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 = $1.602\,19 \times 10^{-19}$ 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 Å (angstrom) = 100 pm

1 M = 1 mol dm^{-3}

pi(π) = 3.142

General data and fundamental constants

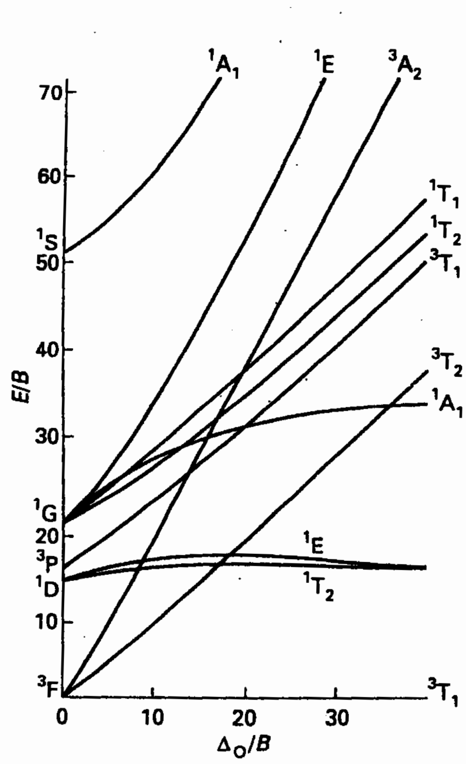
Quantity	Symbol	Value
Speed of light	c	$2.997\,925 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = eN_A$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = kN_A$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ 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	$R_\infty = m_e e^4/8h^3c\varepsilon_0^2$	$1.097\,37 \times 10^{5}$ cm^{-1}

pi(π) = 3.142

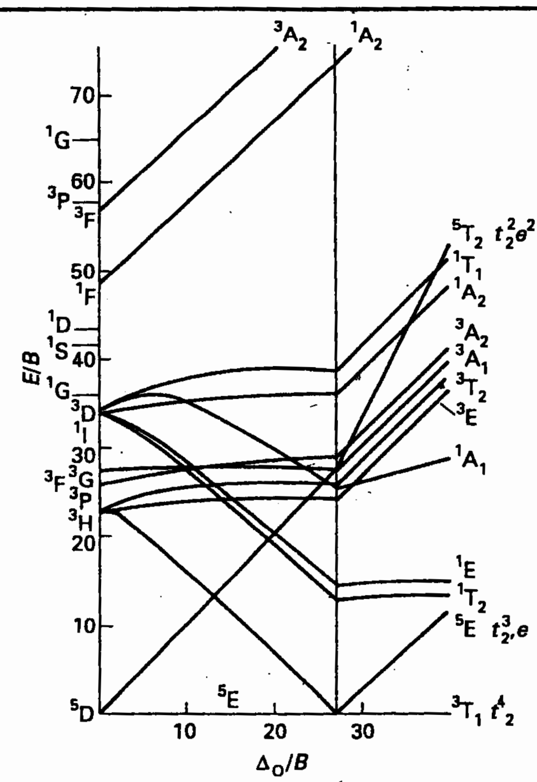
Prefixes

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}

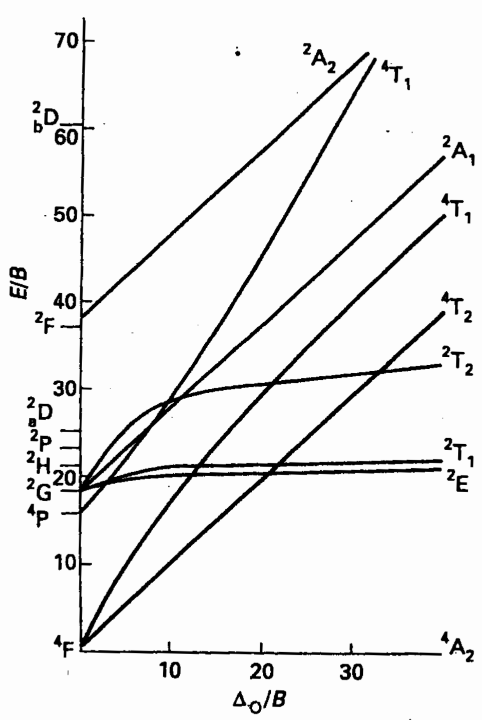
1. d^2 with $C = 4.42B$



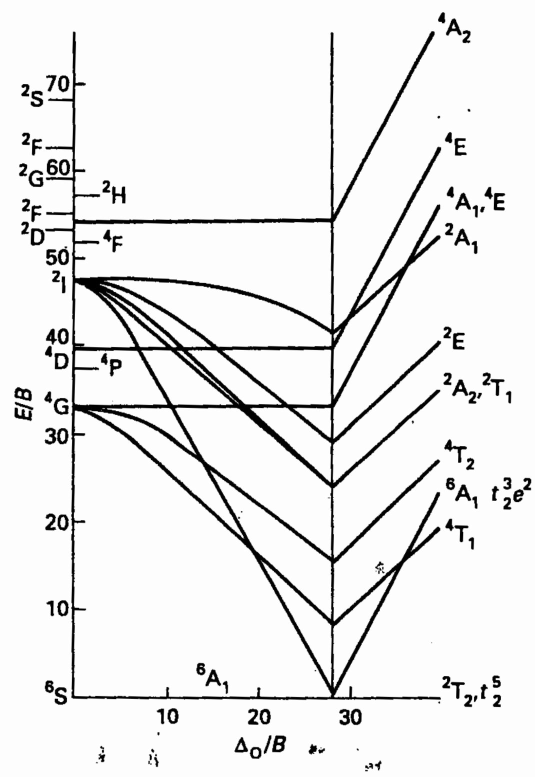
3. d^4 with $C = 4.61B$



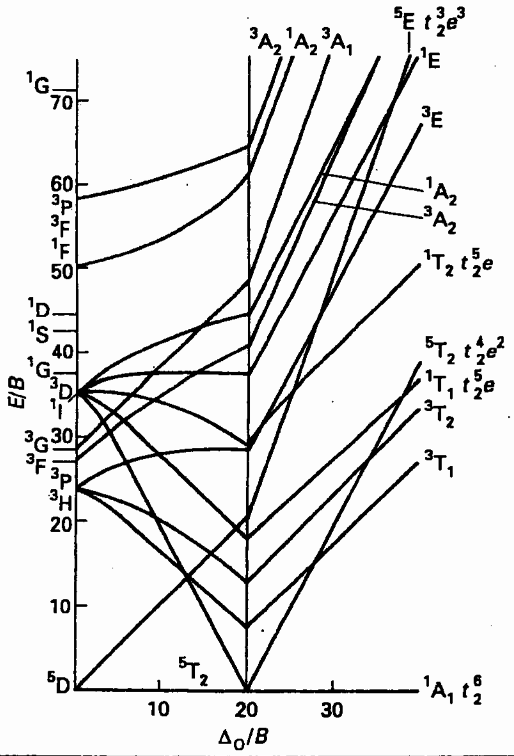
2. d^3 with $C = 4.5B$



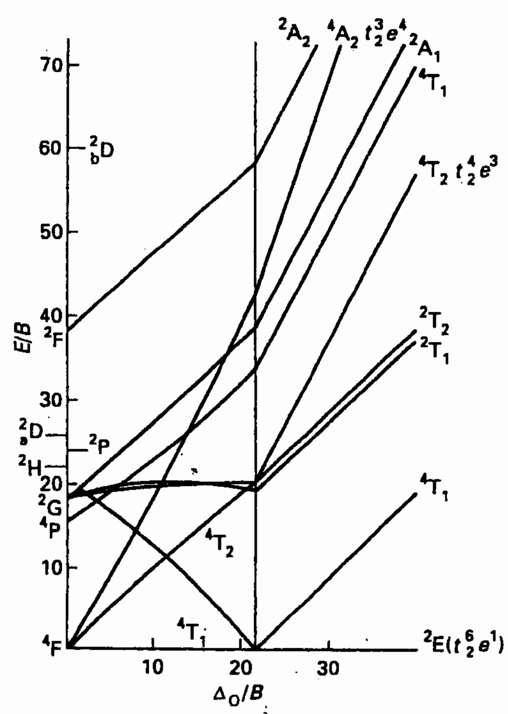
4. d^5 with $C = 4.477B$



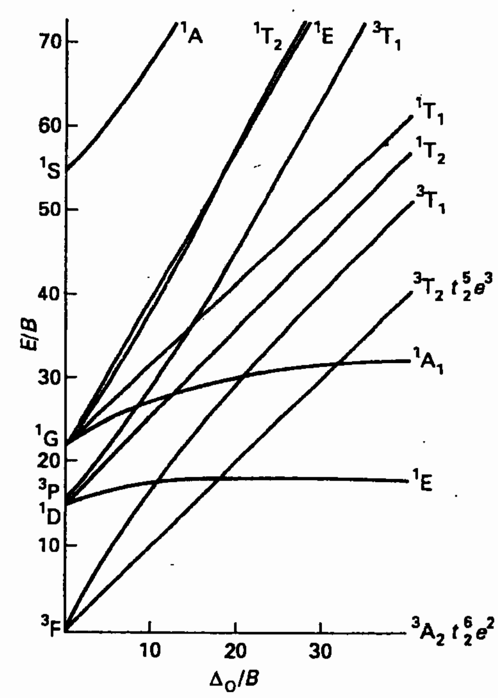
5. d^6 with $C = 4.8B$



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



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



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)	

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$		
A_1'	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	1	−1	1	1	1	−1	R_z	
E_1'	2	2 cos 72°	2 cos 144°	0	2	2 cos 72°	2 cos 144°	0	(x, y)	
E_2'	2	2 cos 144°	2 cos 72°	0	2	2 cos 144°	2 cos 72°	0		(x^2-y^2, xy)
A_1''	1	1	1	1	−1	−1	−1	−1		
A_2''	1	1	1	−1	−1	−1	−1	1	z	
E_1''	2	2 cos 72°	2 cos 144°	0	−2	−2 cos 72°	−2 cos 144°	0	(R_x, R_y)	(xz, yz)
E_2''	2	2 cos 144°	2 cos 72°	0	−2	−2 cos 144°	−2 cos 72°	0		

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	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	−1	−1	R_z	
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1		
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1		
E_{1g}	2	1	−1	−2	0	0	2	1	−1	−2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	−1	−1	2	0	0	2	−1	−1	2	0	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1		
B_{2u}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1		
E_{1u}	2	1	−1	−2	0	0	−2	−1	1	2	0	0	(x, y)	
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0		

TABLE 9.3 Splitting of One-Electron Levels in Various Symmetries

Type of Level	Symmetry of O_h	Symmetry of T_d
s	a_{1g}	a_1
p	t_{1u}	t_2
d	$e_g + t_{2g}$	$e + t_2$
f	$a_{2u} + t_{1u} + t_{2u}$	$a_2 + t_1 + t_2$
g	$a_{1g} + e_g + t_{1g} + t_{2g}$	$a_1 + e + t_1 + t_2$
h	$e_u + 2t_{1u} + t_{2u}$	$e + t_1 + 2t_2$
i	$a_{1g} + a_{2g} + e_g + t_{1g} + 2t_{2g}$	$a_1 + a_2 + e + t_1 + 2t_2$

Table 11.15

Splitting of d^n terms in an octahedral field

Term	Components in an octahedral field
[illegible]	[illegible]