Second Semester Examination
2020/2021 Academic Session

July 2021

KTT212 – Inorganic Chemistry II

Duration: 3 hours

Please check that this examination paper consists of **FOURTEEN (14)** pages of printed materials before you begin the examination.

Answer **Five (5)** questions only. **SECTION A** is **COMPULSARY.** Answer any **TWO (2)** questions from **SECTION B.**

Answer each question on a new page.

If a candidate answered more than five questions, only the answers to the first five questions in the answer sheet will be graded.

Appendix: Tanabe-Sugano Diagram
Flow chart for Determined Molecular Point Groups
Character Tables

SECTION A

COMPULSORY questions.

1. (a) Determine the oxidation state, coordination number of the metal center and the name of the following complexes according to the IUPAC rules.

   (i) $K_2[Cd(CN)_4]$
   (ii) $[Co(H_2O)_6][Ag(CN)_2]_3$
   (iii) $K_2[OsCl_5N]$

(10 marks)

   (b) Explain Werner's Theory using $CoCl_3.4NH_3$ and $CoCl_3.3NH_3$ as examples.

(5 marks)

   (c) A student treated aqueous solutions of $[Rh(NH_3)_4Cl_2]Cl$ with excess $AgNO_3$(*aq*) and $K_2[TiCl_6]$ with excess $AgNO_3$(*aq*) in separate experiments. Predict the student's observation in both experiments and explain.

(5 marks)

2. (a) Cobalt complexes $[Co(CN)_6]^{3-}$ and $[CoF_6]^{3-}$ absorb at 430 nm and 650 nm, respectively. Determine

   (i) the crystal field splitting Δ_o for both complexes in unit of Joule; and

   (ii) the color of the metal.

(8 marks)

   (b) Find the LFSE in terms of D_q and calculate the spin-only magnetic moment (in unit of Bohr-magneton) for the following complexes:

   (i) *cis*–diaqua–*cis*–dichloro–*cis*–difluorocobaltate(II) ion

   (ii) *trans*–dichlorotetrakis(triphenylphosphine)nickel(II)

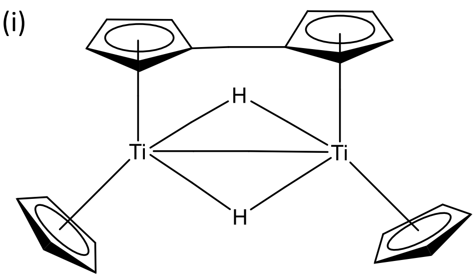
   (iii) tris(bipyridine)ruthenium(II) ion

   (iv) *cis*–dicyanobis(oxalato)manganate(II) ion

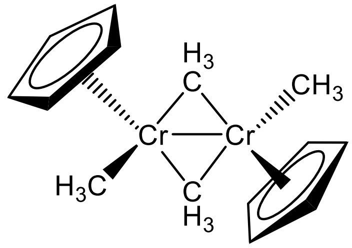
(12 marks)

3. (a) Calculate the number of electrons in the following complexes using covalent model.

(i)



(ii)



(10 marks)

(b) The *trans*-effect is a measurable ground state effect observed in some square planar complexes.

(i) Describe how you would measure this effect in square planar $Pt(PEt_3)_2Cl_2$ complex if you could not obtain an X-ray crystal structure.

(ii) Describe briefly how the *trans*-effect contributes to the variation of ground state energy.

(10 marks)

SECTION B

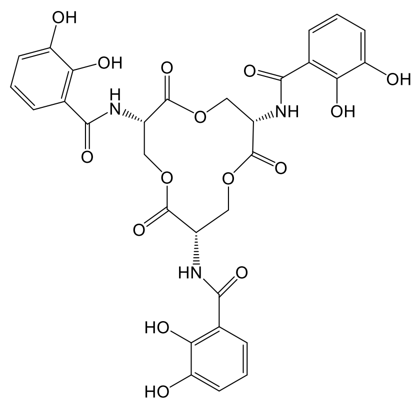
Answer any **TWO (2)** questions.

4. (a) $[IrCl(PMe_3)_3]$ complex (where PMe_3 is trimethylphosphine) is reacted, by a reaction known as 'oxidative addition', with Cl_2 to form octahedral complexes.

i. Draw the isomers of the formed octahedral complexes.
ii. Provide the IUPAC name of the isomers in (i)

(5 marks)

(b) Certain bacteria transport iron(III) into their cells using a compound known as enterobactin. The binding took place when the enterobactin is deprotonated. The formation constant for the iron(III)-enterobactin complex is about 10^{49}. Based on the given structure of enterobactin, provide a reason why the formation constant is so high.



(5 marks)

(c) The molecule $[Fe(CO)_4Cl_2]$ possesses a point group of C_{2v}.

i. Derive the reducible representation of $\Gamma_{Fe\text{-}CO}$ (Fe-CO as basic function).

ii. Demonstrate how the reducing formula can be applied to obtain the irreducible representations for Fe-CO and Fe-Cl.

(10 marks)

5. (a) Prove that the following reaction took place through inner sphere coordination mechanism.

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} + 5H_2O \longrightarrow [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5Cl]^{2+} + 5NH_3$$

(6 marks)

(b) Suggest a pathway to indicate the transfer of an electron over the bridging ligand in (a).

(4 marks)

(c) Describe briefly Molecular Orbital Theory based on the transition metal-ligand complexes with octahedral geometry.

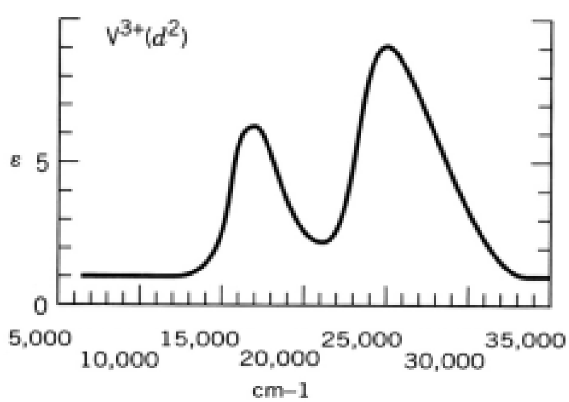
(10 marks)

6. (a) Demonstrate that the product of K_1 to K_4 for the stepwise replacement of water in $[Cu(H_2O)_4]^{2+}$ by ammonia result in the expression for

$$\beta_4 = \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(H_2O)_4]^{2+}][NH_3]^4} .$$

(10 marks)

(b) The electronic spectrum of $[V(H_2O)_6]^{3+}$ is shown as follows:

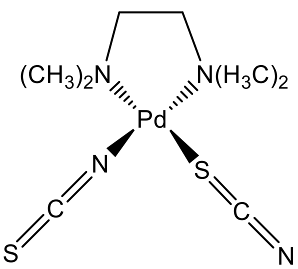


i. Suggest the probable transitions for the two bands based on Tanabe-Sugano diagram.

ii. Determine the values of Racah parameter, B and crystal field splitting energy, Δ_o.

(10 marks)

7. (a) The ambidentate ligands in the coordination complex below bond through different ends to the metal center. Elaborate.



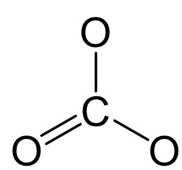
(5 marks)

(b) Provide two (2) examples of metal complexes that contains carbon rings with extended π-systems. Determine the number of electrons according to ionic model that obey 18 electron rules.

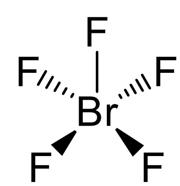
(5 marks)

(c) For each of the following molecules, provide

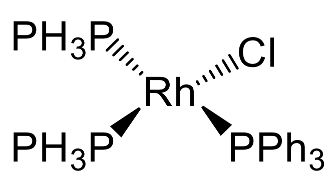
(i) symmetrical elements
(ii) point group



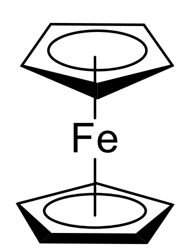
I



II



III



IV

(10 marks)

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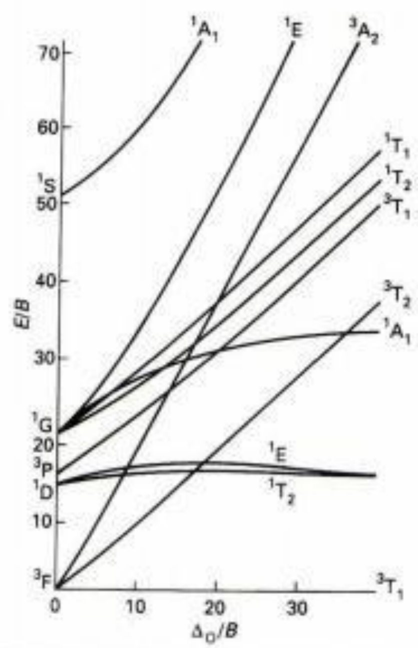
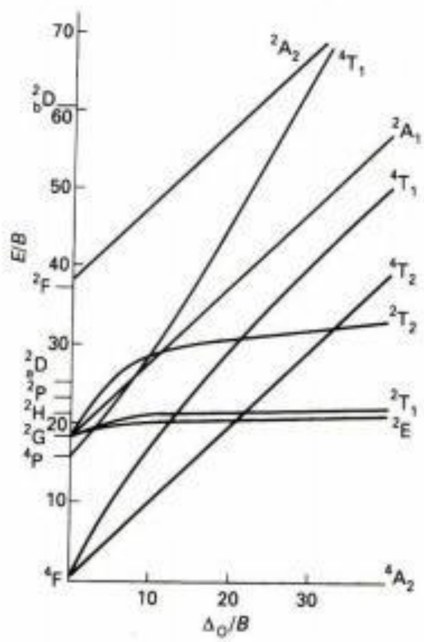
TANABE-SUGANO DIAGRAM

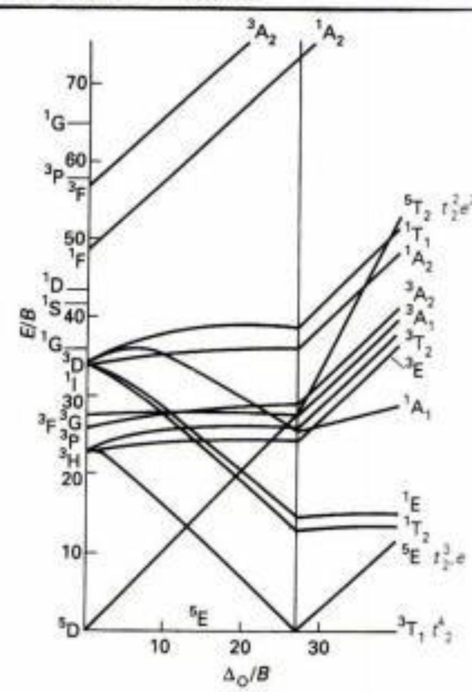
1. d^1 with $C = 4.42B$



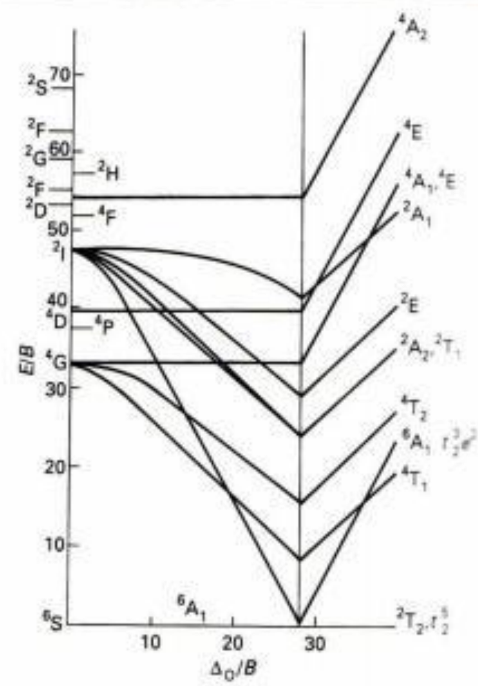
2. d^3 with $C = 4.5B$



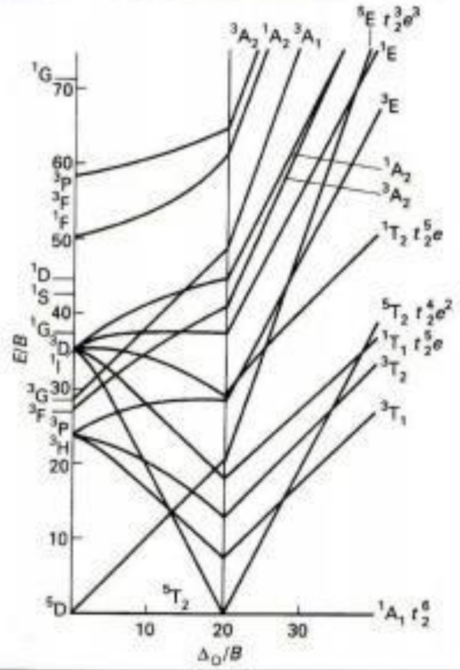
3. d^4 with $C = 4.61B$



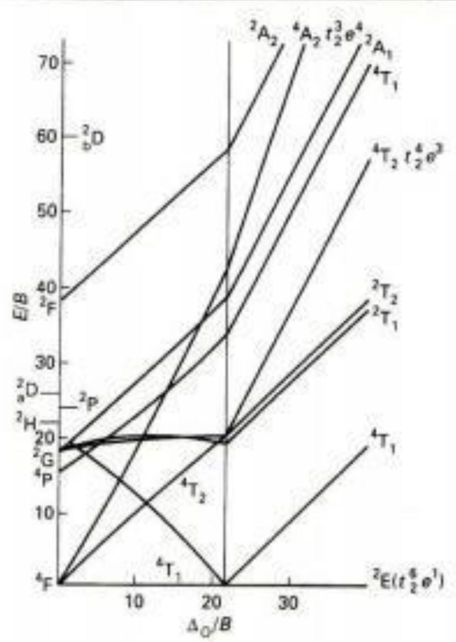
4. d^5 with $C = 4.477B$



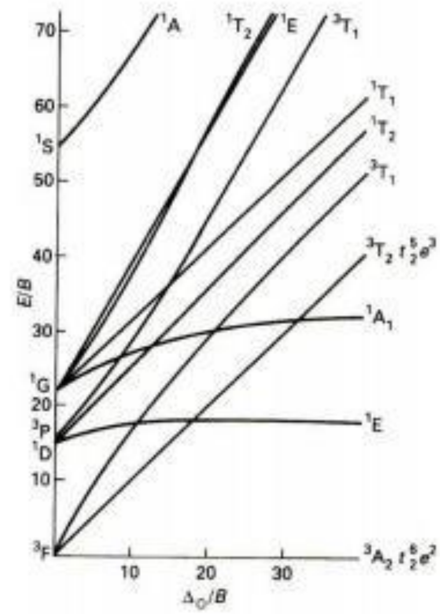
5. d^6 with $C = 4.8B$



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



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



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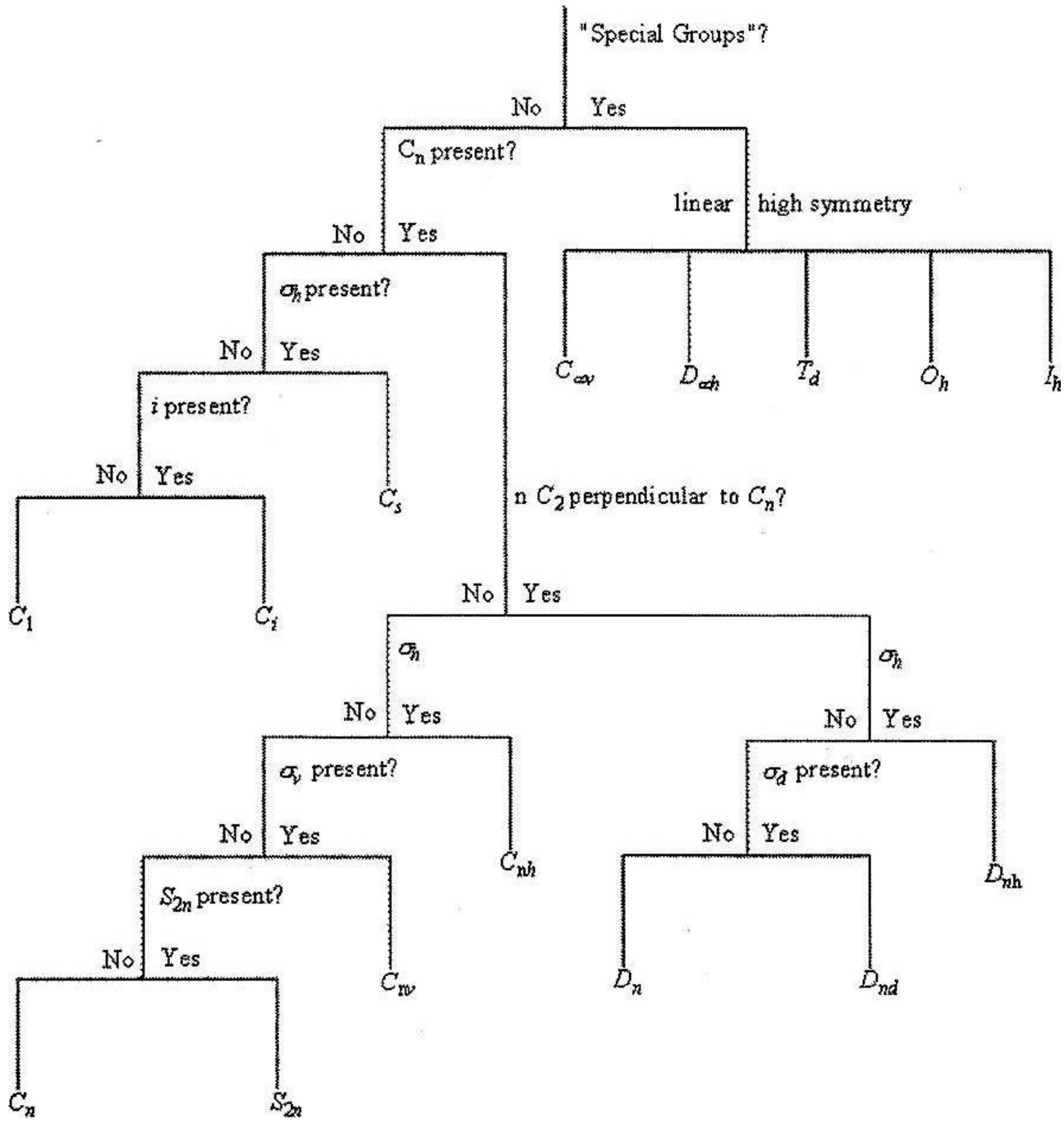
Flow Chart for Determining Molecular Point Groups



Character Tables for selected point groups

C_s	E	σ_h		
A'	1	1	x,y,R_z	x^2,y^2,z^2,xy
A"	1	-1	z,R_x,R_y	yz,xz

C_i	E	i		
A_g	1	1	R_x,R_y,R_z	x^2,y^2,z^2,xy,xz,yz
A_u	1	-1	x,y,z	

C_2	E	C_2		
A	1	1	z,R_z	x^2+y^2,z^2
B	1	-1	x,y,R_x,R_y	yz,xz

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A	1	1	1	1		x^2,y^2,z^2, xy
B_1	1	1	-1	-1	z,Rz	xy
B_2	1	-1	1	-1	y, Ry	xz
B_3	1	-1	-1	1	x,Rx	yz

D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		x^2+y^2, z^2
A_2	1	1	-1	z,R_z	
E	2	-1	0	$(x,y);(R_x,R_y)$	(xz,yz); (x^2-y^2,xy)

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_z	
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)

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	

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	2cos72°	2cos144°	0	2	2cos72°	2cos144°	0	(x,y)	
E_2'	2	2cos144°	2cos72°	0	2	2cos144°	2cos72°	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	2cos72°	2cos144°	0	-2	-2cos72°	-2cos144°	0	(R_x, R_y)	(xz, yz)
E_2''	2	2cos144°	2cos72°	0	-2	-2cos144°	-2cos72°	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		x^2-y^2
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		xy
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		
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		

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		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	z	xy
E	2	0	-2	0	0	(x,y); (R_x,R_y)	(xz,yz)

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	-1	1	1	-1	R_z	
E_g	2	-1	0	2	-1	0	(R_x,R_y)	$(x^2-y^2,xy);(xz,yz)$
A_{1u}	1	1	1	-1	-1	-1		
A_{2u}	1	1	-1	-1	-1	1	z	
E_u	2	-1	0	-2	1	0	(x,y)	

S_4	E	S_4	C_2	S_4^3		
A	1	1	1	1	R_z	x^2+y^2, z^2
B	1	-1	1	-1	z	x^2-y^2, xy
E	1	±i	-1	-(_i)	(x,y); (R_x,R_y)	(xz,yz)

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x,y,z)	(xz,yz.xy)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ $(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
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		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2,x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x,R_y,R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz,yz,xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x,y,z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Appenidix B. Constants & Useful Energy Conversions

Planck's Constant, $h = 6.626 \times 10^{-34}$ J-s
Boltzman's Constant, $k = 1.381 \times 10^{-23}$ J/K = 0.6950 cm^{-1}/K
speed of light, $c = 2.998 \times 10^{8}$ m/s

1 eV = 1.60219×10^{-19} J = 96.485 kJ/mol = 22.58 kcal/mol = 8065.5 cm^{-1}
1 cm^{-1} = 11.96 J/mol = 2.859 cal/mol = 0.1240 meV

Some Direct Products Note that is some instances, g and u must be added (gxg=uxu=g; gxu=u), some subscripts must be omited and ' and " must be added ('x' = " x" = '; ' x " =")

D_2, D_{2h}	A	B_1	B_2	B_3
A	A	B_1	B_2	B_3
B_1		A	B_3	B_2
B_2			A	B_1
B_3				A

C_{2v}	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2		A_1	B_2	B_1
B_1			A_1	A_2
B_2				A_1

$C_{3v}, D_3, D_{3d}, D_{3h}$	A_1	A_2	E
A_1	A_1	A_2	E
A_2		A_1	E
E			A_1+[A_2]+E

C_4, C_{4h}, S_4	A	B	E
A	A	B	E
B		A	E
E			[A]+A+E

$C_{4v}, D_4, D_{2d}, D_{4h}$	A_1	A_2	B_1	B_2	E
A_1	A_1	A_2	B_1	B_2	E
A_2		A_1	B_2	B_1	E
B_1			A_1	A_2	E
B_2				A_1	E
E					A_1+[A_2]+B_1+B_2

C_{5v}, , D_5, $D_{5h;5d}$	A_1	A_2	E_1	E_2
A_1	A_1	A_2	E_1	E_2
A_2		A_1	E_1	E_2
E_1			A_1+[A_2]+E_2	E_1+E_2
E_2				A_1+[A_2]+E_1

C_6, C_{6h}	A	B	E_1	E_2
A	A	B	E_1	E_2
B		A	E_2	E_1
E_1			[A]+A+E_2	2B+E_1
E_2				[A]+A+E_2

C_{6v}, D_6, D_{6h}	A_1	A_2	B_1	B_2	E_1	E_2
A_1	A_1	A_2	B_1	B_2	E_1	E_2
A_2		A_1	B_2	B_1	E_1	E_2
B_1			A_1	A_2	E_2	E_1
B_2				A_1	E_2	E_1
E_1					A_1+[A_2]+E_2	B_1+B_2+E_1
E_2						A_1+[A_2]+E_2

O_h, T_d	A_1	A_2	E	T_1	T_2
A_1	A_1	A_2	E	T_1	T_2
A_2		A_1	E	T_2	T_1
E			A_1+[A_2]+E	T_1+T_2	T_1+T_2
T_1				A_1+E+[T_1]+T_2	A_2+E+T_1+T_2
T_2					A_1+E+[T_1]+T_2

…14/-

Standard Valence Orbital H_{ii} values (eV)

Atom	ns	np	(n-1)d	n
H	-13.6			1
B	-15.2	-8.5		2
C	-21.4	-11.4		
N	-26.0	-13.4		
O	-32.3	-14.8		
F	-40.0	-18.1		
Si	-17.3	-9.2		3
P	-18.7	-14.0		
S	-20.0	-13.3		
Cl	-26.3	-14.2		
Sc	-8.9	-2.8	-8.5	4
Ti	-9.0	-5.4	-10.8	
V	-8.8	-5.5	-11.0	
Cr	-8.7	-5.2	-11.2	
Mn	-9.8	-5.9	-11.7	
Fe	-9.1	-5.3	-12.6	
Co	-9.2	-5.3	-13.2	
Ni	-9.2	-5.2	-13.5	
Cu	-11.4	-6.1	-14.0	
Zn	-12.4	-6.5		
Ga	-14.6	-6.8		
Ge	-16.0	-9.0		
As	-16.2	-12.2		
Se	-20.5	-13.2		
Br	-22.7	-13.1		
Mo	-8.3	-5.2	-10.5	5
Ru	-10.4	-6.9	-14.9	
Rh	-3.09	-4.6	-12.5	
Pd	-7.3	-3.8	-12.0	
Sb	-18.8	-11.7		
I	-18.0	-12.7		
Te	-20.8	-13.2		6
W	-8.3	-5.2	-10.4	
Re	-9.36	-6.0	-12.7	
Os	-8.5	3.5	-11.0	
Pt	-9.1	-5.5	-12.6	
Au	-10.9	-5.6	-15.1	