UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2017/2018

TITLE OF PAPER: CHEMICAL APPLICATIONS OF GROUP THEORY

COURSE NUMBER: CHE321

TIME ALLOWED: TWO (2) HOURS

INSTRUCTIONS: THERE ARE Five (5) QUESTIONS.
ANSWER ANY FOUR (4) QUESTIONS.
EACH QUESTION IS WORTH 25 MARKS.

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"

THE FOLLOWING HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER:

- Periodic Table of the Elements
- Table of Universal Constants
- Character tables for C_{2v}, C_{4v} and D_{2h} point groups
- Decision Tree (Flow chart) for point groups

Question One

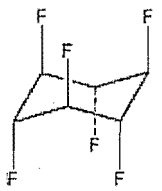
a) List the symmetry elements of the molecules that are given below. For each case, the location of the symmetry elements should be indicated in the diagram.

i) PF_5, trigonal bipyramidal
ii) Ethylene, $H2C{=}CH_2$
iii) *Cis*-$[Co(NH_3)_4Cl_2]$, (ignore H atoms)

[9]

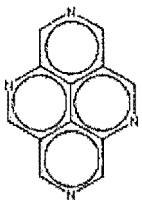
b) Use the accompanying flow-chart diagram (decision tree), to determine the correct point group symbol for each of the systems below.

i)



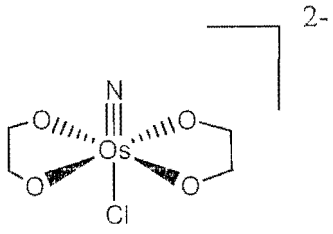
[4]

ii)



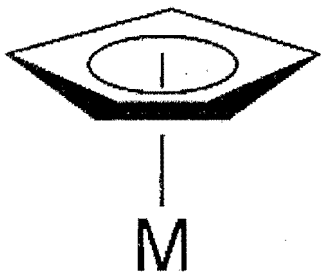
[4]

iii)



[4]

iv)



[4]

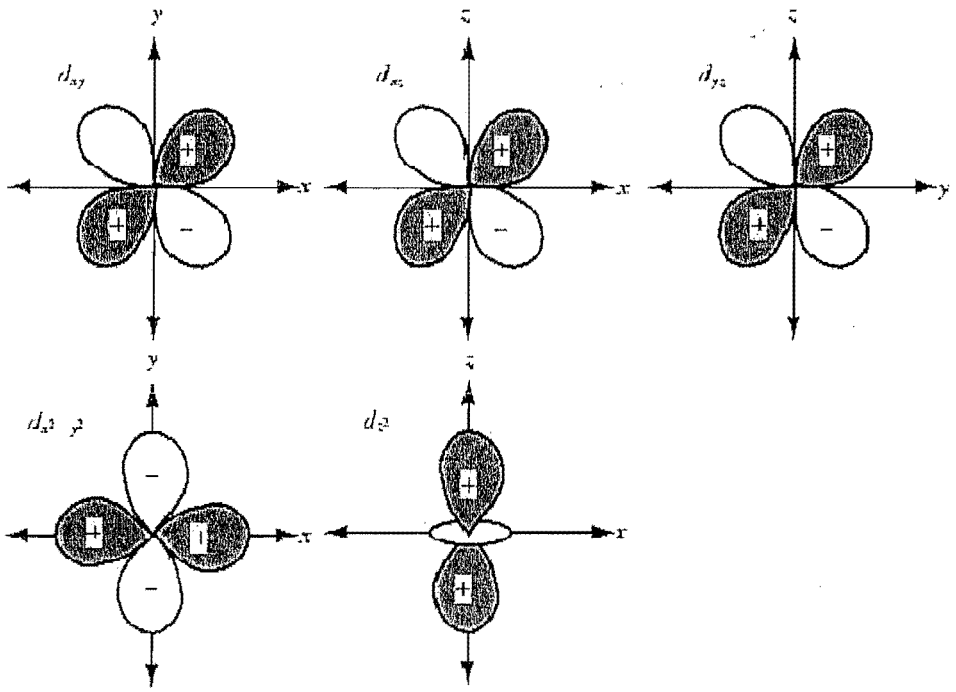
Question Two

The C_{2h} character table is in part:

C_{2h}	E	C_2	i	σ_h
A_g	1	1	1	1
B_g	1	-1	1	-1
A_u	1	1	-1	-1
B_u	1	-1	-1	1

a) Consider trans-1,2-dichloroethylene, ClHC=CClH, of C_{2h} symmetry. Taking the C_2 axis as the z axis and σ_h to be in the xy plane, obtain the reducible representation arising from taking x, y and z axes as the basis set. Decompose the reducible representation into irreducible representations. [Note: Derivation of matrices is not required]. **[10]**

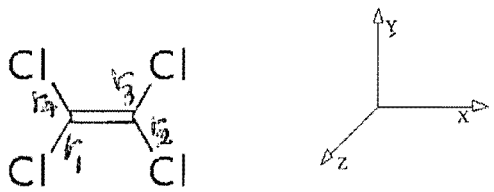
b) To which irreducible representation does each of the five d orbitals belong in C_{2h} symmetry? [The diagrams of the five d orbitals are given below].



[15]

Question Three

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, answer questions that follow. [Note: The z axis is perpendicular to the molecular plane and the page]



a) Determine symmetries of all the C-Cl stretching modes of vibration for the molecule **[8]**

b) Determine which of the species are IR active and which ones are Ra active **[3]**

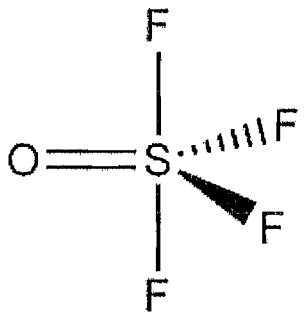
c) Find the SALC's of the stretching modes of vibration from above **[10]**

d) Use the information in iii) above to sketch the stretching modes of vibration **[4]**

[4]

Question Four

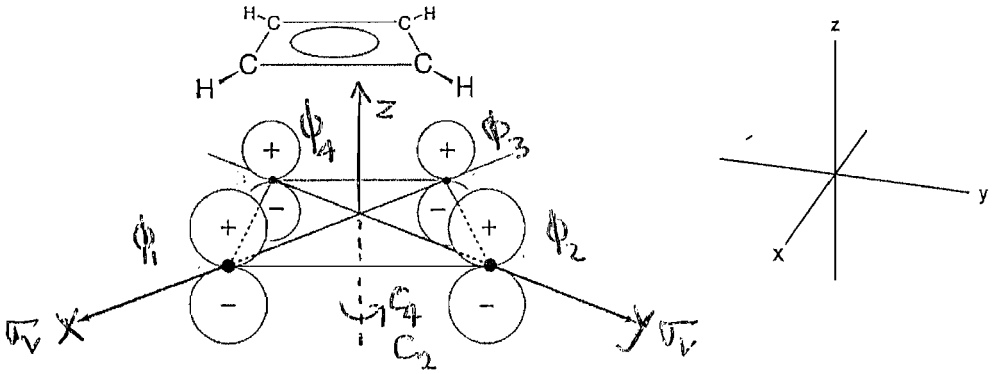
The structure of thionyl tetrafluoride $S(=O)F_4$ (C_{2v} symmetry), can be diagrammed as below. Let the basis set for ligand sigma-type orbitals be s_1, s_2, s_3, s_4, s_5 with s_1 being assigned to the oxygen sigma-type orbital. Let the C_2 axis coincide with the S=O bond. Use the accompanying C_{2v} character table to determine possible hybridization schemes around the sulphur atom.



[25]

Question Five

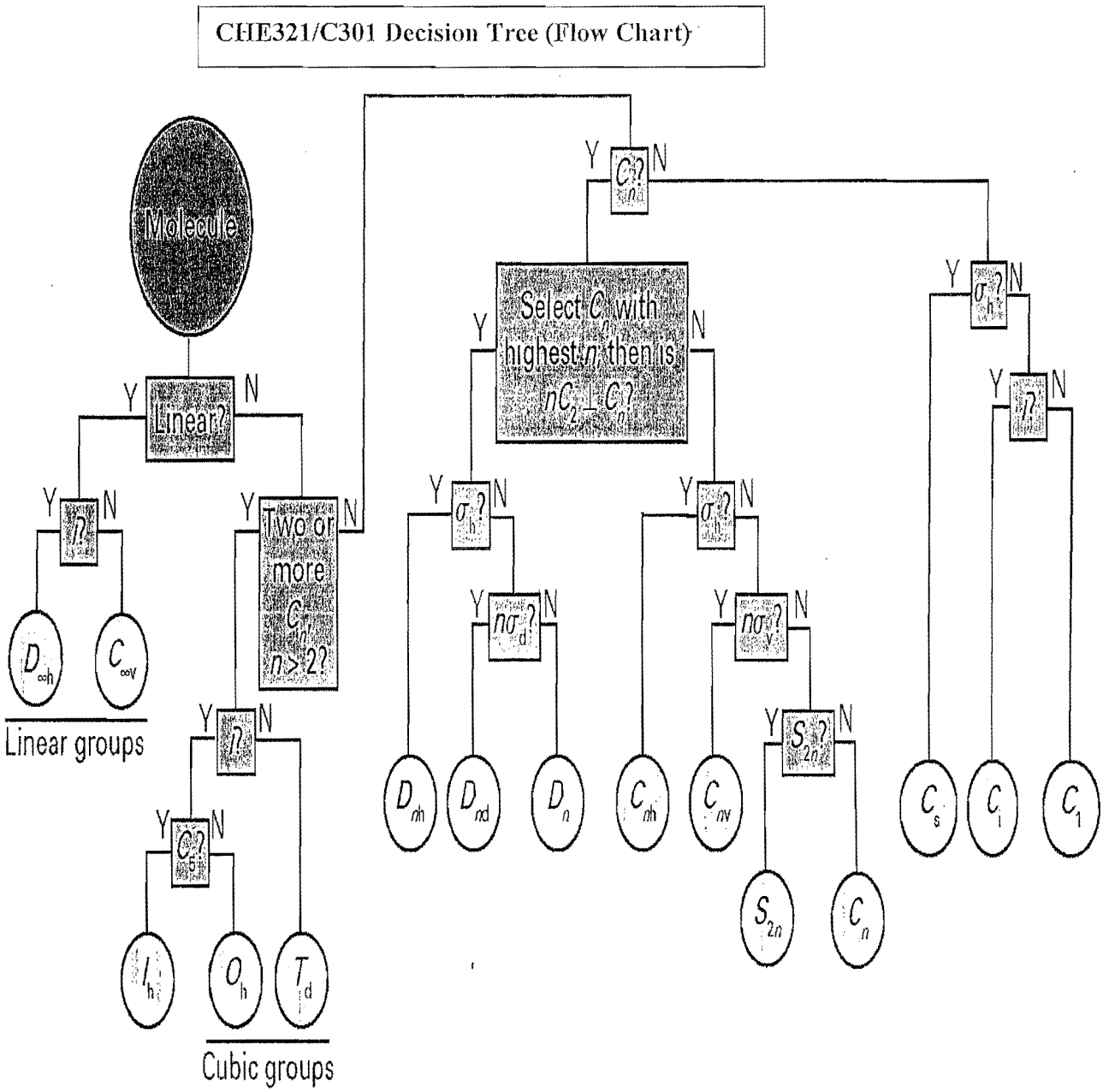
Some unstable organic molecules are stabilized by complexing with a transition metal atom, as in the complex $C_4H_4Fe(CO)_3$, where the "C_4H_4" fragment is cyclobutadiene. The idealized structure of the organic molecule is shown in the diagram below, together with its π-type atomic orbitals (that are involved in π bonding). The coordinate system is such that the z axes is perpendicular to the plane of the molecule.



Let the four pi-type orbitals (Φ_1, Φ_2, Φ_3, Φ_3, Φ_4) constitute a basis set. For the sake of simplicity, let us assume the molecule has <u>C_{4v} **symmetry**</u>.

a) Determine the reducible representation for the basis set and decompose it into irreducible representations **[10]**

b) Determine symmetry-adapted linear combinations of the basis set **[15]**



The flow-chart (Decision tree) used for assigning point groups

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PERIODIC TABLE OF THE ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 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											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	116.71 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 ^{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.

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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_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)

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	

The C_{nh} groups

C_{2h}	E	C_2	i	σ_h
A_g	1	1	1	1
B_g	1	−1	1	−1
A_u	1	1	−1	−1
B_u	1	−1	−1	1