UNIVERSITY OF SWAZILAND

RE-SIT 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.

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

NON-PROGRAMMABLE ELECTRONIC CALCULATORS MAY BE USED

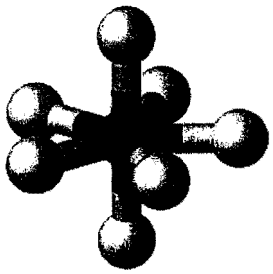
PLEASE DO NOT OPEN THIS PAPER UNTIL AUTHORISED TO DO SO BY THE CHIEF INVIGILATOR.

"Marks will be awarded for method, clearly labelled diagrams, organization and presentation of thoughts in clear and concise language"

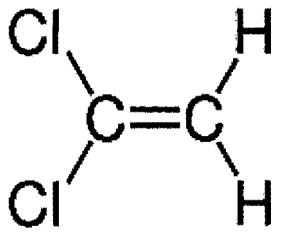
Question One

List the symmetry elements of the molecules that are given below. For each case, the symbol and the location of the principal axis should be indicated in the diagram.

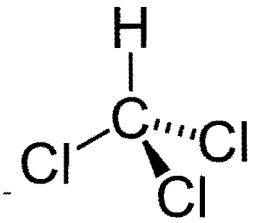
a) IF_7



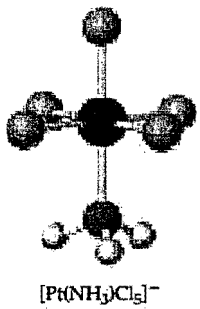
b) *1,1*-dichloromoethene



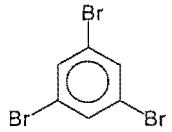
c) Chloroform molecule



d) $[Pt(NH_3)Cl_5]^-$, (ignore H atoms)

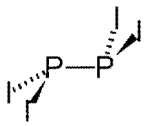


e)



f)

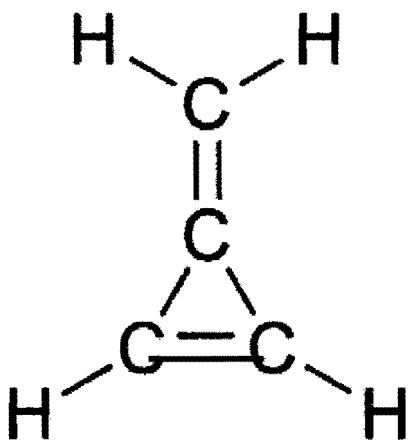
g)



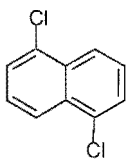
Question Two

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

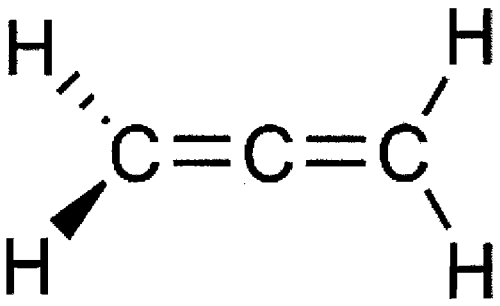
a)



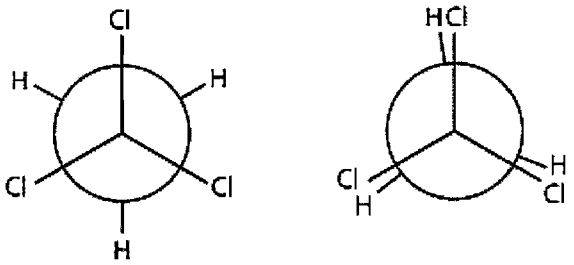
b) 1,5-dichloronaphthalene



c)

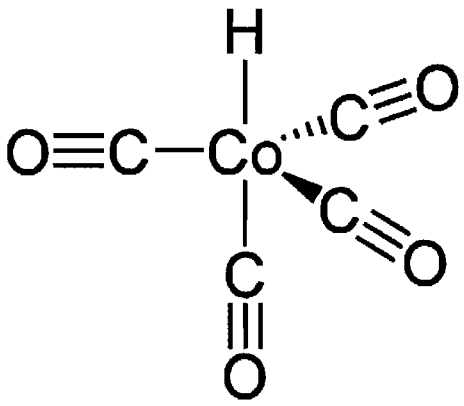


d) Both conformers



Staggered Eclipsed

e)



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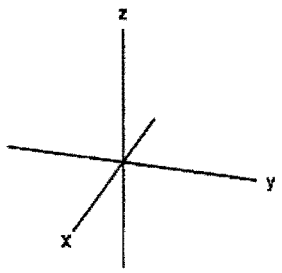
Question Three

Consider the three Cartesian coordinates, x, y and z on the O atom of a water molecule (C_{2v} point group) such that the z axis coincides with the C_2 symmetry element.



Let the Cartesian coordinates above form the basis set:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Use the given basis set above to answer the following questions

a) Determine the matrix M(R) corresponding to each operation R in the C_{2v} point group
b) Determine the character X(R) for each operation R
c) Give the reducible representation Γ_R for the basis set
d) Use the reduction formula to determine the irreducible representations that correspond to the basis set (i.e., belonging to Γ_R).
e) Check for consistency of your result with the character table

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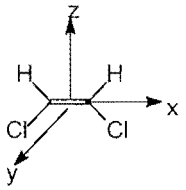
Question Four

a) Obtain a set of transformation matrices to describe the effect of each symmetry operation in the C_{2v} point group on a set of coordinates x,y,z at the point indicated in the diagram. [*The **point** is at the **origin** of the three axes at the **mid-point** of the **double bond**. The **xz** plane **coincides** with the **plane** of the molecule*).



b) Use internal coordinates to determine irreducible representations for stretching C-H vibrations of the molecule, and indicate whether they are IR and/or Ra active

c) Use internal coordinates to determine irreducible representations for stretching C-Cl vibrations of the molecule, and indicate whether they are IR and/or Ra active

d) Using the projection operator method, determine the SALCs for the C-H and C-Cl stretching vibrations. Sketch the results.

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Question Five

Consider the SiF_4 molecule. The four F atoms are in a tetrahedral structure with T_d symmetry.

a) Give the reducible representation (Γ_σ) for the fluorine sigma-type orbitals.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_σ					

b) Reduce the reducible representation and determine the silicon orbitals used for bonding in SiF_4

c) Give possible hybridization scheme(s) for SiF_4. Note that the four F atoms require four atomic orbitals from Si for bonding.

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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						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.

Fundamental Physical Constants (six significant figures)

Avogadro's number	N_A	$= 6.02214 \times 10^{23}$/mol
atomic mass unit	amu	$= 1.66054 \times 10^{-27}$ kg
charge of the electron (or proton)	e	$= 1.60218 \times 10^{-19}$ C
Faraday constant	F	$= 9.64853 \times 10^{4}$ C/mol
mass of the electron	m_e	$= 9.10939 \times 10^{-31}$ kg
mass of the neutron	m_n	$= 1.67493 \times 10^{-27}$ kg
mass of the proton	m_p	$= 1.67262 \times 10^{-27}$ kg
Planck's constant	h	$= 6.62607 \times 10^{-34}$ J·s
speed of light in a vacuum	c	$= 2.99792 \times 10^{8}$ m/s
standard acceleration of gravity	g	$= 9.80665$ m/s^2
universal gas constant	R	$= 8.31447$ J/(mol·K)
		$= 8.20578 \times 10^{-2}$ (atm·L)/(mol·K)

Rydberg constant = 1.097×10^{7} m^{-1}

SI Unit Prefixes

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

Conversions and Relationships

Length
SI unit: meter, m

1 km = 1000 m
= 0.62 mile (mi)
1 inch (in) = 2.54 cm
1 m = 1.094 yards (yd)
1 pm = 10^{-12} m = 0.01 Å

Volume
SI unit: cubic meter, m^3

1 dm^3 = 10^{-3} m^3
= 1 liter (L)
= 1.057 quarts (qt)
1 cm^3 = 1 mL
1 m^3 = 35.3 ft^3

Pressure
SI unit: pascal, Pa

1 Pa = 1 N/m^2
= 1 kg/m·s^2
1 atm = 1.01325×10^{5} Pa
= 760 torr
1 bar = 1×10^{5} Pa

Mass
SI unit: kilogram, kg

1 kg = 10^{3} g
= 2.205 lb
1 metric ton (t) = 10^{3} kg

Energy
SI unit: joule, J

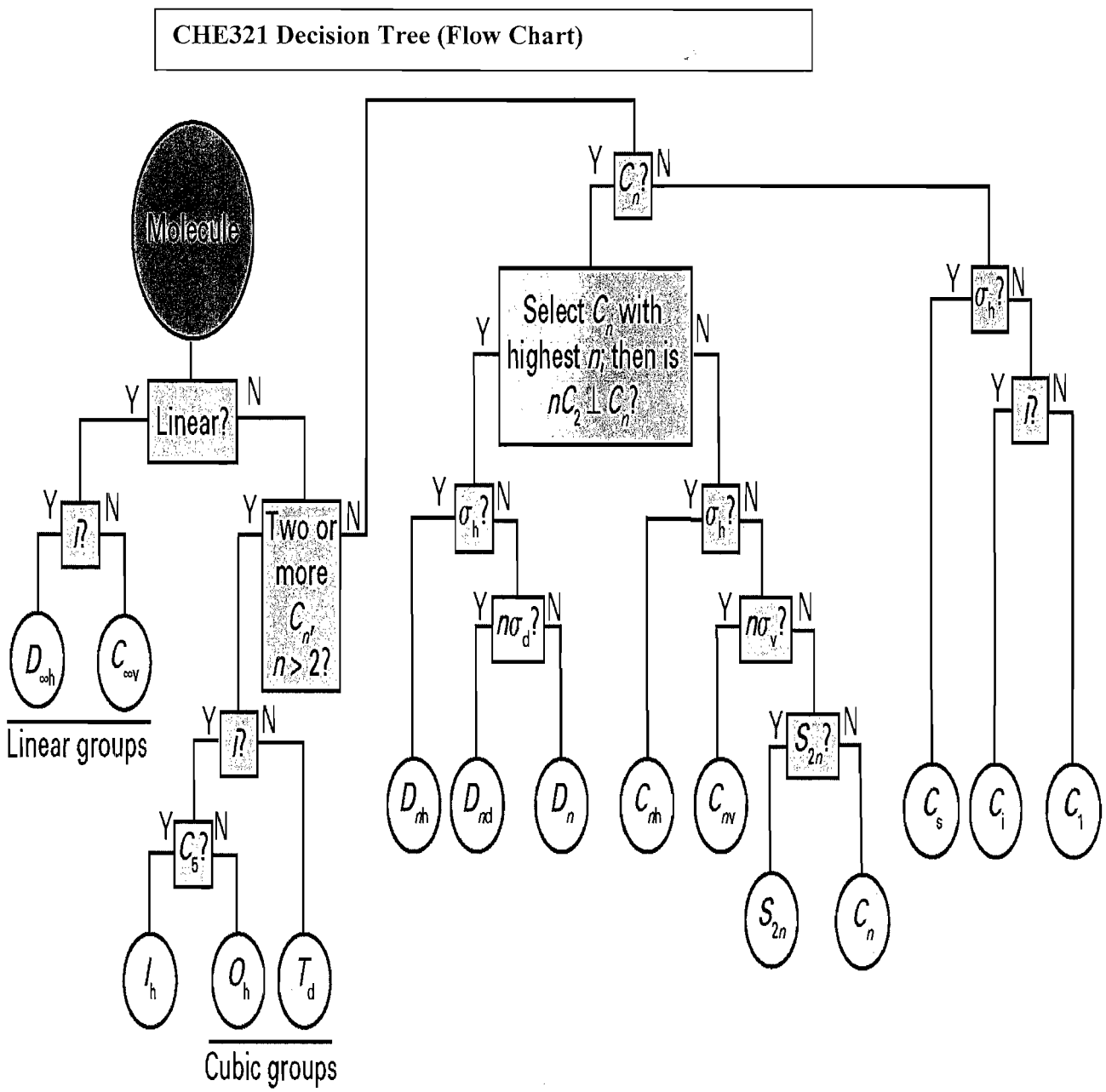
1 J = 1 kg·m^2/s^2
= 1 coulomb·volt (1 C·V)
1 cal = 4.184 J
1 eV = 1.602×10^{-19} J

Math relationships

$\pi = 3.1416$
volume of sphere = $\frac{4}{3}\pi r^3$
volume of cylinder = $\pi r^2 h$

Temperature
SI unit: kelvin, K

0 K = −273.15°C
mp of H_2O = 0°C (273.15 K)
bp of H_2O = 100°C (373.15 K)
T (K) = T (°C) + 273.15
T (°C) = $[T\,(°F) - 32]\frac{5}{9}$
T (°F) = $\frac{9}{5}T$ (°C) + 32



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

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Character tables for point groups C_{2v} and T_d

C_{2v}	E	C_2 (z)	σ_v (xz)	σ_v (yz)	linear functions, rotations	quadratic functions	cubic functions
A_1	**+1**	**+1**	**+1**	**+1**	z	x^2, y^2, z^2	z^3, x^2z, y^2z
A_2	**+1**	**+1**	**-1**	**-1**	R_z	xy	xyz
B_1	**+1**	**-1**	**+1**	**-1**	x, R_y	xz	xz^2, x^3, xy^2
B_2	**+1**	**-1**	**-1**	**+1**	y, R_x	yz	yz^2, y^3, x^2y

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	+1	-	$x^2+y^2+z^2$	xyz
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)	-	$[x(z^2-y^2), y(z^2-x^2), z(x^2-y^2)]$
T_2	+3	0	-1	-1	+1	(x, y, z)	(xy, xz, yz)	(x^3, y^3, z^3) $[x(z^2+y^2), y(z^2+x^2), z(x^2+y^2)]$