UNIVERSITY OF SWAZILAND

SUPPLEMENTARY FINAL EXAMINATION

ACADEMIC YEAR 2010/2011

TITLE OF PAPER: INORGANIC CHEMISTRY

COURSE CODE: 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.

CALCULATORS MAY BE USED

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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) $W(CH_2CH_3)_6$

[6]

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 six-coordinate complexes, and draw structures of the isomers:

i) $[Pt(en)_2Cl_2]Br_2$
ii) $Pd(bpy)(NCS)_2$
iii) $Rh(acac)_3$

[13]

Question Two

a) A monomeric complex of cobalt gave the following result on analysis:

Species	Co	NH_3	Cl^-	SO_4^{2-}	H_2O
%, by mass	21.24	24.77	12.81	34.65	?

The compound is diamagnetic and contains no other groups or elements, except that water might be present. Using the above data, calculate the formula of the compound

[8]

b) The value of μ_{eff} for $[CoF_6]^{3-}$ is 5.63 BM. 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.

[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) A substitution reaction of *trans*-$[Pt(PEt_3)_2(Ph)Cl]$ with thiourea, tu, that leads to the formation of *trans*-$[Pt(PEt_3)_2(Ph)(tu)]$ in methanol, follows a two-term rate law with

$$k_{obs} = k_I + k_2[tu]$$

Give a plausible mechanism for the reaction. Suggest how the values of k_I and k_2 may be obtained.

[10]

b) $[V(H_2O)_6]^{3+}$ has absorption bands at 17800, 25700 and 34500 cm^{-1}. Use the Tanbe-Sugano diagram for a d^2 configuration to estimate values of Δ_o and B for this complex.

[15]

Question Four

a) Complete and balance the following reactions:

i) $Cr + Cl_2 \longrightarrow$

ii) $Mo + Cl_2 \longrightarrow$

iii) $Cr + O_2 \longrightarrow$

iv) $Mo + O_2 \longrightarrow$

[8]

b) Explain each of the following:

i) TiO_2 is white but $TiCl_3$ is violet

[4]

ii) Physical and chemical properties of Zr and Hf are much more similar than the properties of Zr and Ti

[4]

c) Write a balanced reaction equation to depict what happens when vanadium(V) oxide, V_2O_5, is dissolved in

i) A concentrated solution of a strong base
ii) A concentrated solution of a strong acid

[4]

d) Iron(III) iodide, FeI_3, is unstable whereas $FeCl_3$ is stable. Explain. Give a balanced reaction equation depicting the reaction that takes place when an aqueous solution of KI is added to an aqueous solution of $Fe(NO_3)_3$

[5]

Question Five

a) Consider the reaction of $[Rh(H_2O)_6]^{3+}$ (which has octahedral shape) with chloride ions, Cl^-. Use the concept of ***trans effect*** to give the structure of the product when careful addition of Cl^- to the hexaaqua complex is carried out so that there are (per complex)

i) two Cl^- ions

ii) three Cl^- ions

iii) four Cl^- ions

[Note the trans effect sequence: $H_2O < Cl^-$]

[6]

b) Explain why

i) Certain ligands such as F^- stabilize the maximum oxidation states of elements whilst others such as CO stabilize the lowest oxidation states. Illustrate your answer with suitable orbital diagrams

[8]

ii) The lowest oxide of a transition metal tends to be basic whereas the highest oxidation state tends to acidic

[3]

c) Discuss, with examples (one for each), the difference between outer-sphere and inner-sphere mechanisms. State what is meant by a self-exchange mechanism.

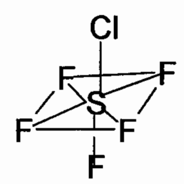
[8]

Question Six

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

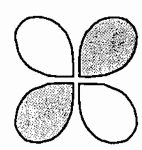
i) Cis-$[PtCl_2BrI]^{2-}$

ii) SF_5Cl



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

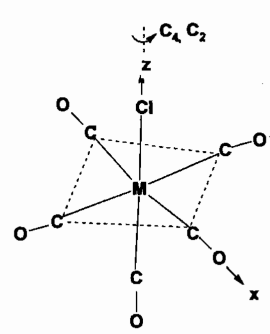
iv) d_{xy} orbital (whose shape is sketched below)



[12]

b) Determine the symmetries of CO **stretching modes** for the complex $[M(CO)_5Cl]$ (which has C_{4v} point group). Which of the modes are IR active? Which ones are Raman active?

[13]



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

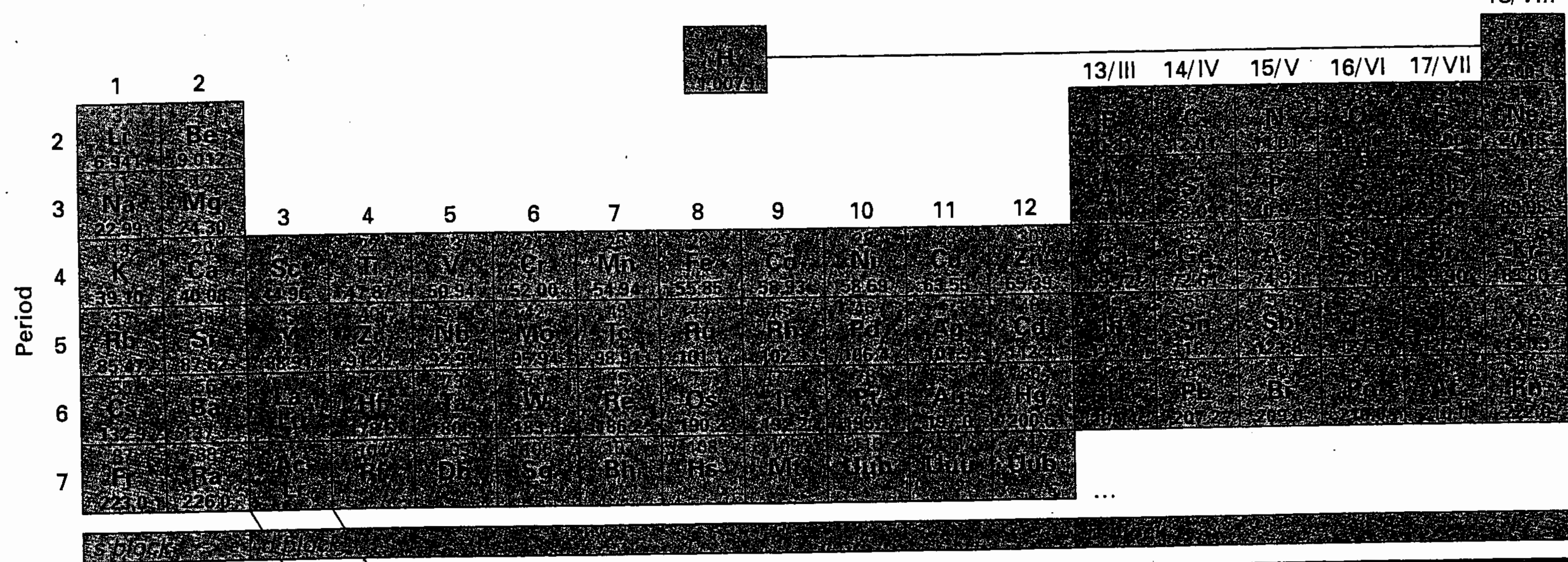
Quantity	Symbol	Value
Speed of light	c	$2.997\,925 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = eN_A$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = kN_A$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78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

The Periodic Table

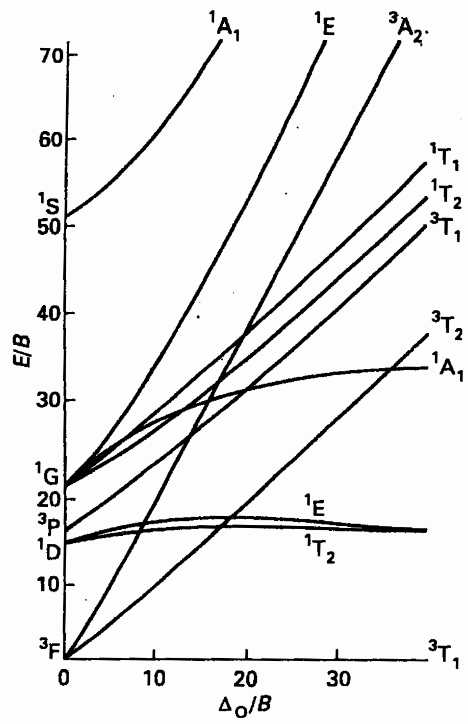


	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Lanthanides	**La** 138.9	**Ce** 140.1	**Pr** 140.9	**Nd** 144.2	**Pm** 146.9	**Sm** 150.4	**Eu** 152.0	**Gd** 157.2	**Tb** 158.9	**Dy** 162.5	**Ho** 164.9	**Er** 167.3	**Tm** 168.9	**Yb** 173.0	**Lu** 175.0
	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
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** 256.1	**No** 259.1	**Lr** 260.1

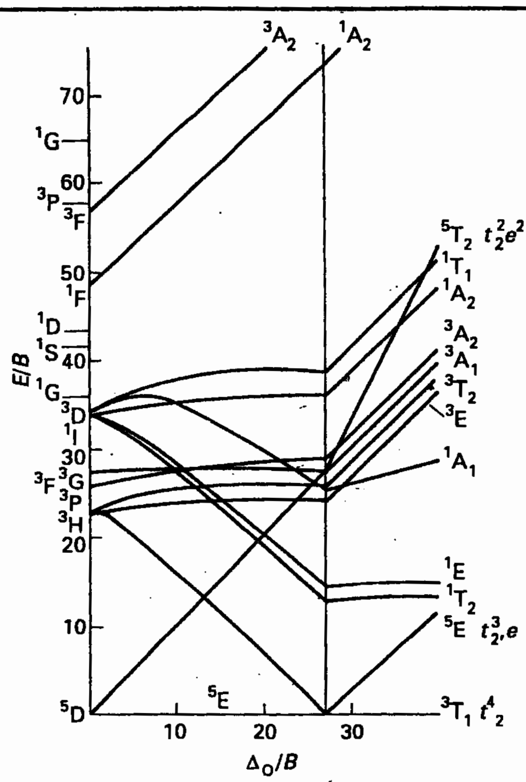
f block

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

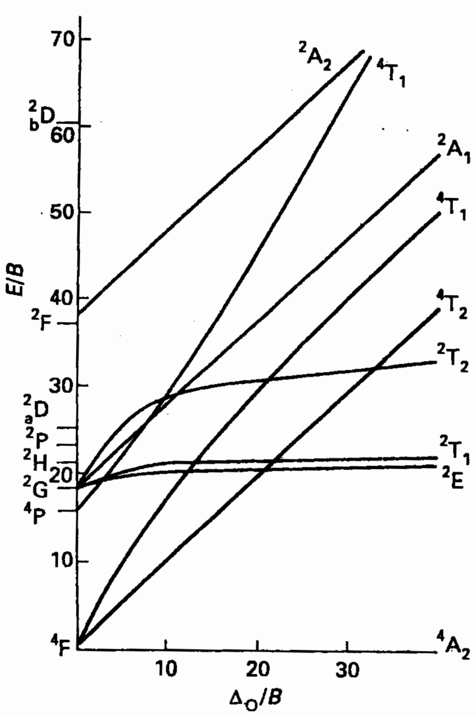
d^2



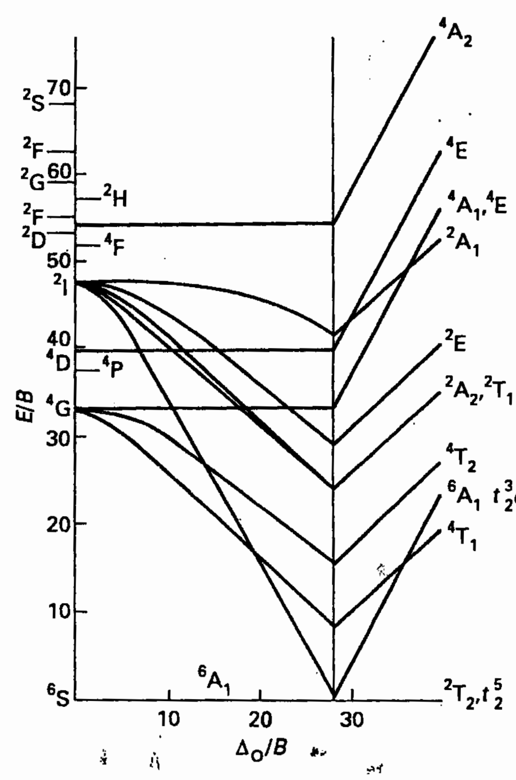
3. d^4 with $C = 4.61B$



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



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



4. The C_{nv} Groups

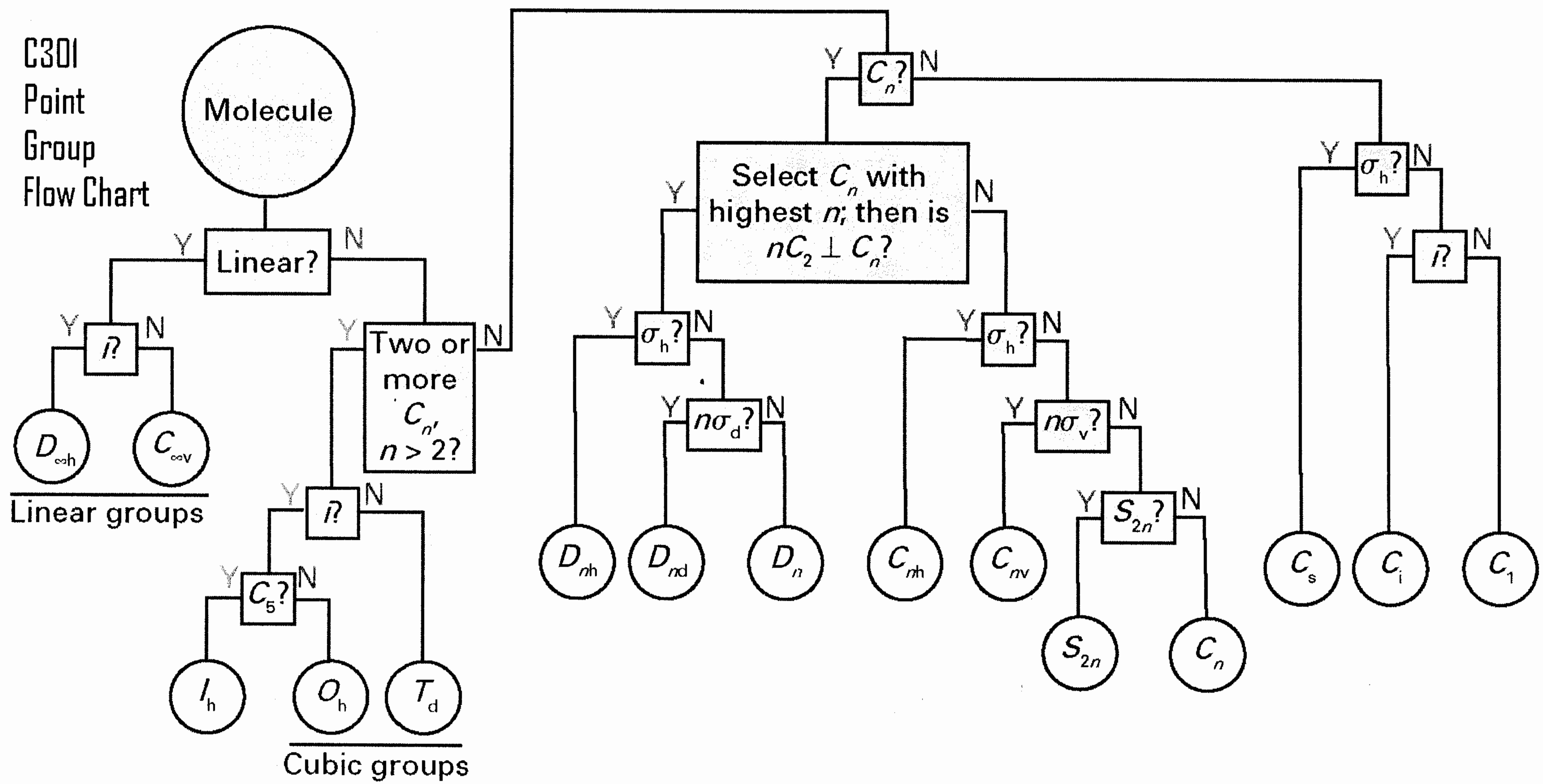
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

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_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_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$		
A_1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	R_z	
E_1	2	2 cos 72°	2 cos 144°	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	2 cos 144°	2 cos 72°	0		$(x^2 - y^2, xy)$

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$		
A_1	1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	1	−1	−1	R_z	
B_1	1	−1	1	−1	1	−1		
B_2	1	−1	1	−1	−1	1		
E_1	2	1	−1	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	−1	−1	2	0	0		$(x^2 - y^2, xy)$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Point
Group
Flow Chart
Molecule
Linear?
Y
N
i?
$D_{\infty h}$
$C_{\infty v}$
Linear groups
Two or more C_n, $n > 2$?
i?
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