UNIVERSITY OF SWAZILAND

SUPPLEMENTARY FINAL EXAMINATION

ACADEMIC YEAR 2014/2015

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.

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.

Question One

a) Give the IUPAC name for each of the following:

i) $K_3[Co(NO_2)_6]$
ii) $[Cr(en)_3]^{3+}[Cr(Ox)_3]^{3-}$
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) $RhH_3(PPh_3)_3$

[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.

i) Using the above data, calculate the formula of the compound
ii) Check if there is any water present. If water is present, what is the final formula of the compound?

[8]

b) The magnetic moment for the complex $[CoF_6]^{3-}$ is found to be 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 reaction of *trans*-$[Pt(PEt_3)_2(Ph)Cl]$ with thiourea, tu, in methanol follows a two-term rate law with

$$k_{obs} = k_1 + k_2[tu]$$

Give a plausible mechanism for the reaction. Suggest how the values of k_1 and k_2 may be obtained.

[8]

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

[17]

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) Sketch at least three possible geometries for a complex with coordination number six (CN=6). **[6]**

c) Explain each of the following:

i) TiO_2 is white but $TiCl_3$ is violet

[4]

ii) Iron(VI) oxide is more oxidizing than chromium(VI) oxide.

[4]

e) Write equations to show the reaction of Cr_2O_3 with sulfuric acid

[3]

Question Five

a) Starting with $[Rh(H_2O)_6]^{3+}$ and chloride ion, Cl^-, suggest a method for preparing each of the following:

i) *trans*-$[RhCl_2(H_2O)_4]^+$

ii) *mer*-$[RhCl_3(H_2O)_3]$

iii) *trans*-$[RhCl_4(H_2O)_2]^-$

[7]

b) The electronic spectrum of $[Fe(H_2O)_6]^{2+}$ has one peak which is around 1000 nm. On the other hand, the complex $[Fe(CN)_6]^{4-}$ exhibits at least two absorption bands at lower wave lengths. By using the appropriate Tanabe-Sugano diagram, account for the likely origin of the absorption bands for each of the complexes.

[8]

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.

[7]

d) What reason can you suggest for the sequence Co>Rh>Ir in the rates of H_2O exchange of $[M(H_2O)_6]^{3+}$ ions?

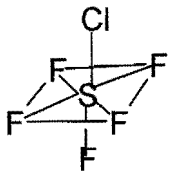
[3]

Question Six

a) With the help of the flow-chart which is provided, determine point group for each of the following:

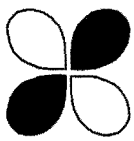
i) Cis-$[PtCl_2BrI]^{2-}$

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 Cr-O **<u>stretching modes</u>** for the complex $[CrO_3X]^-$ (which has C_{3v} point group). Which ones of the modes are IR active? Which ones are Raman active? Show all your work.

[13]

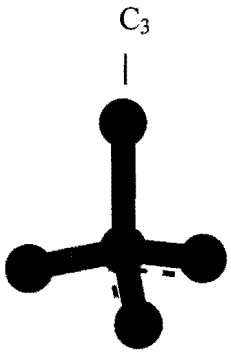


Table of hard, intermediate and soft Acids and Bases

	Ligands (Lewis bases)	Metal centres (Lewis acids)
Hard; class (a)	F^-, Cl^-, H_2O, ROH, R_2O, $[OH]^-$, $[RO]^-$, $[RCO_2]^-$, $[CO_3]^{2-}$, $[NO_3]^-$, $[PO_4]^{3-}$, $[SO_4]^{2-}$, $[ClO_4]^-$, $[ox]^{2-}$, NH_3, RNH_2	Li^+, Na^+, K^+, Rb^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}; Ga^{3+}, In^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Y^{3+}, Th^{4+}, Pu^{4+}, Ti^{4+}, Zr^{4+}, $[VO]^{2+}$, $[VO_2]^+$
Soft; class (b)	I^-, H^-, R^-, $[CN]^-$ (*C*-bound), CO (*C*-bound), RNC, RSH, R_2S, $[RS]^-$, $[SCN]^-$ (*S*-bound), R_3P, R_3As, R_3Sb, alkenes, arenes	Zero oxidation state metal centres, Tl^+, Cu^+, Ag^+, Au^+, $[Hg_2]^{2+}$, Hg^{2+}, Cd^{2+}, Pd^{2+}, Pt^{2+}, Tl^{3+}
Intermediate	Br^-, $[N_3]^-$, py, $[SCN]^-$ (*N*-bound), $ArNH_2$, $[NO_2]^-$, $[SO_3]^{2-}$	Pb^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Os^{2+}, Ru^{3+}, Rh^{3+}, Ir^{3+}

CHARACTER TABLES

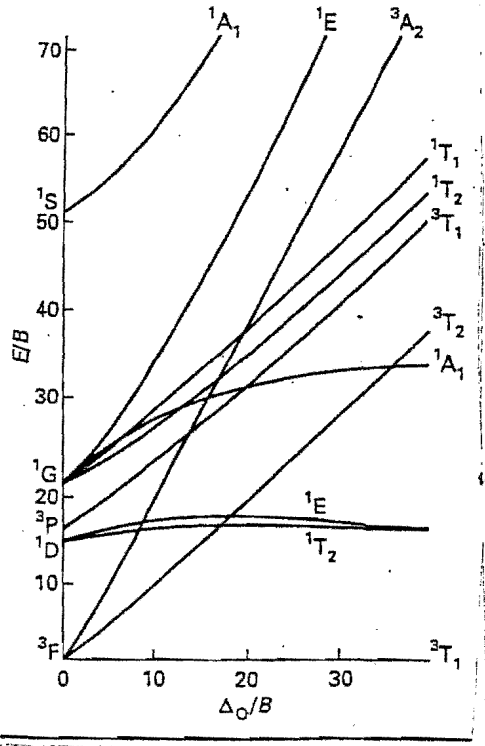
4. The C_{nv} Groups

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

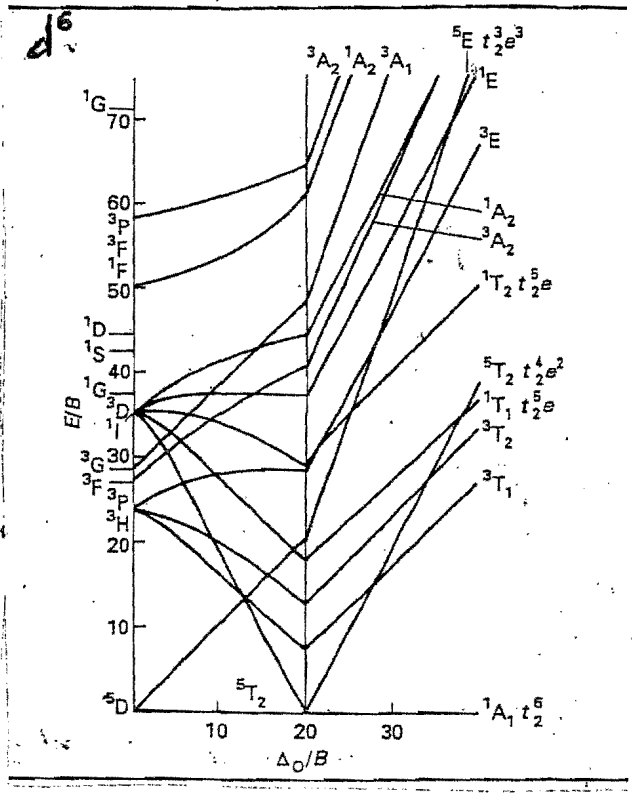
C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

TANABE–SUGANO DIAGRAMS

d^2 with $C = 4.42B$



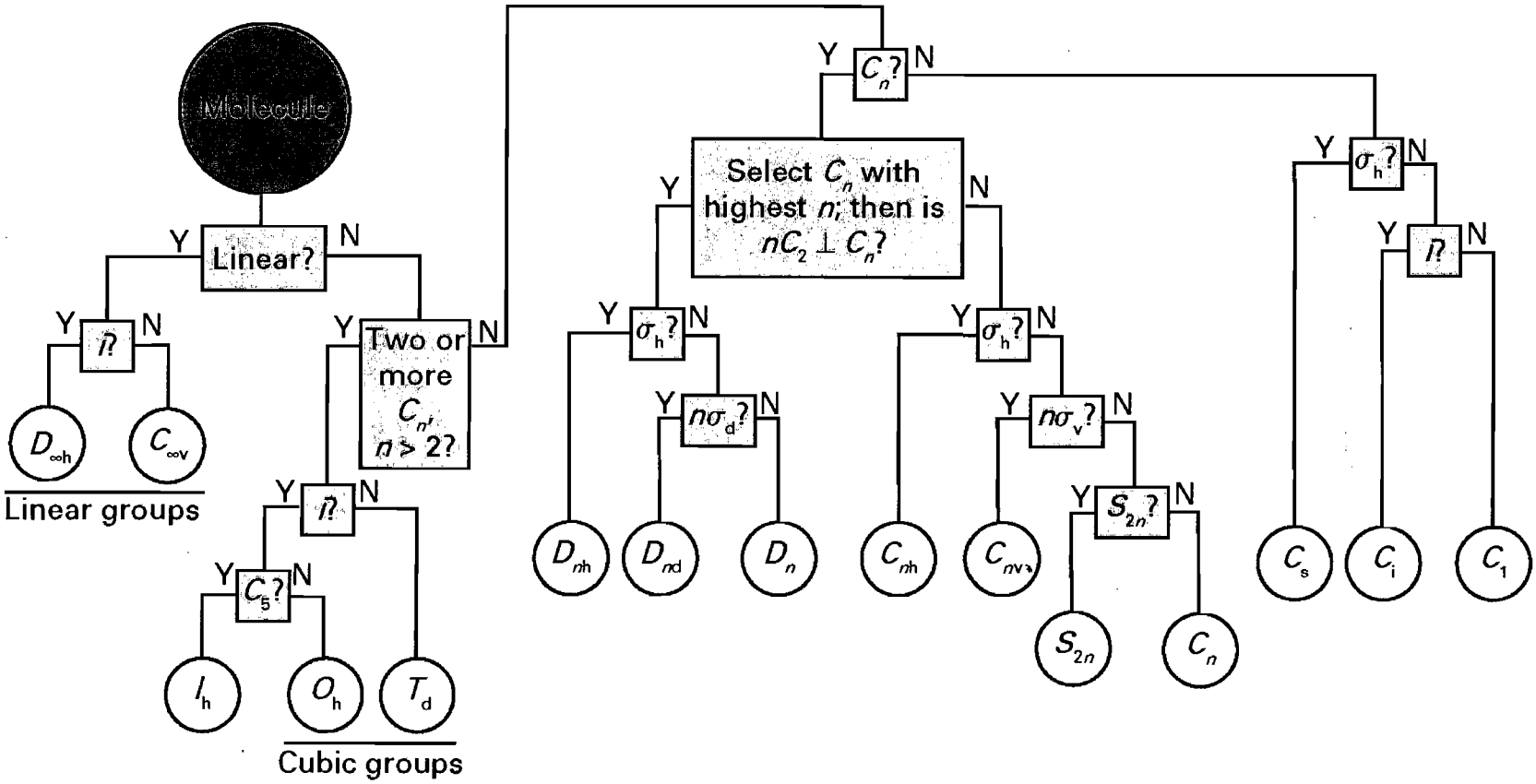
d^6 with $C = 4.8B$

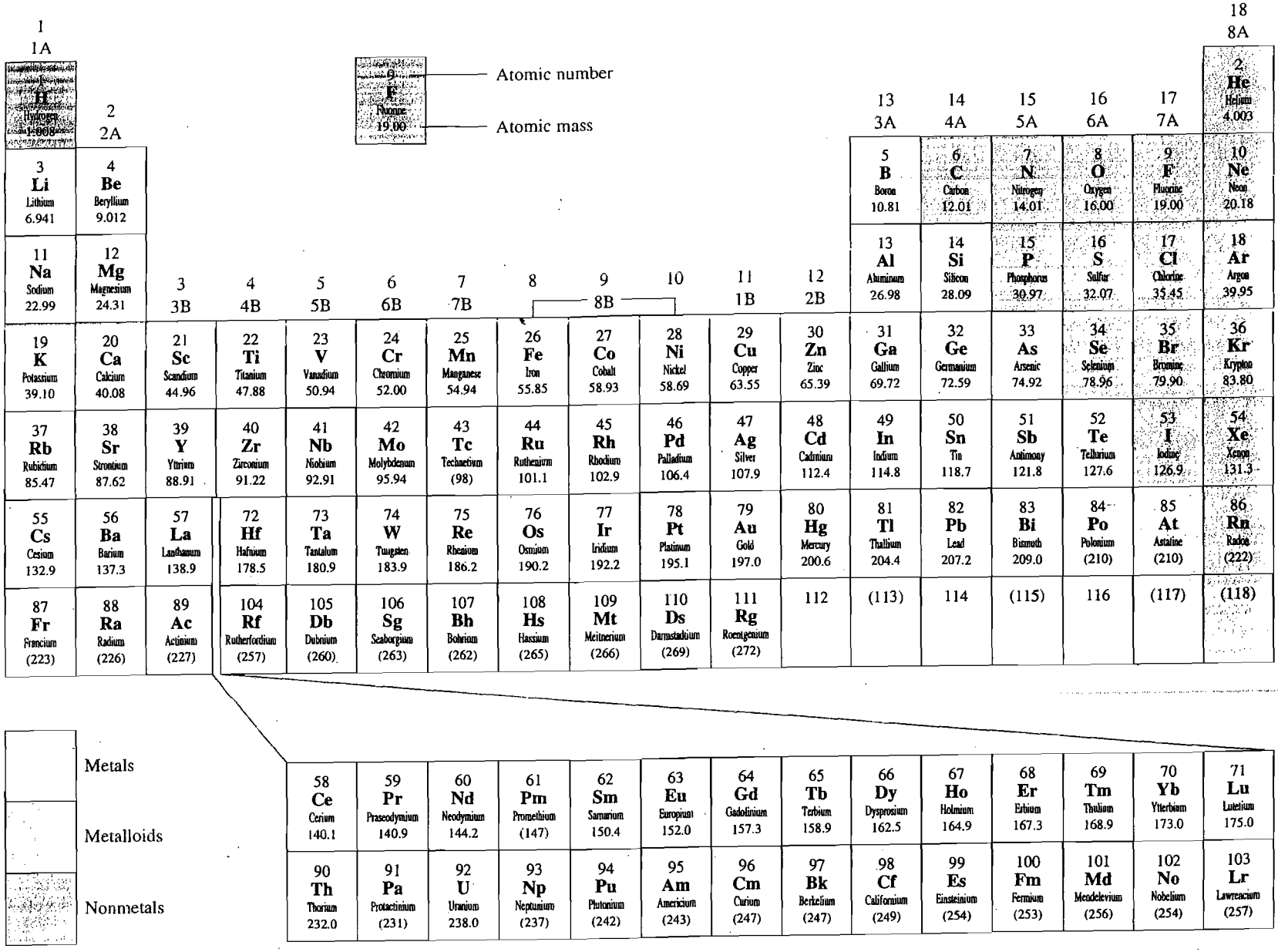


PHYSICAL CONSTANTS

Speed of light in a vacuum	c_0	2.99792458×10^{8} m s^{-1}
Permittivity of a vacuum	ϵ_0	$8.854187816 \times 10^{-12}$ F m^{-1}
	$4\pi\epsilon_0$	1.11264×10^{-10} c^2 N^{-1} m^{-2}
Planck constant	h	$6.6260755(40) \times 10^{-34}$ J s
Elementary charge	e	$1.60217733(49) \times 10^{-19}$ C
Avogadro constant	N_A	$6.0221367(36) \times 10^{23}$ mol^{-1}
Boltzmann constant	k	$1.380658(12) \times 10^{-23}$ J K^{-1}
Gas constant	R	8.314510(70) J K^{-1} mol^{-1}
Bohr radius	a_0	$5.29177249(24) \times 10^{-11}$ m
Rydberg constant	R_c	$1.0973731534(13) \times 10^{7}$ m^{-1} (infinite nuclear mass)
	✓ R_H	1.096777 x 10^{7} m^{-1}
Bohr magneton	μ_B	$9.2740154(31) \times 10^{-24}$ J T^{-1}
	π	3.14159265359
Faraday constant	F	$9.6485309(29) \times 10^{4}$ C mol^{-1}
Atomic mass unit	m_u	$1.6605402(10) \times 10^{-27}$ kg
Mass of the electron	m_e	$9.1093897(54) \times 10^{-31}$ kg or $5.48579903(13) \times 10^{-4}$ m_u
Mass of the proton	m_p	1.007276470(12) m_u
Mass of the neutron	m_n	1.008664904(14) m_u
Mass of the deuteron	m_d	2.013553214(24) m_u
Mass of the triton	m_t	3.01550071(4) m_u
Mass of the α-particle	m_α	4.001506170(50) m_u

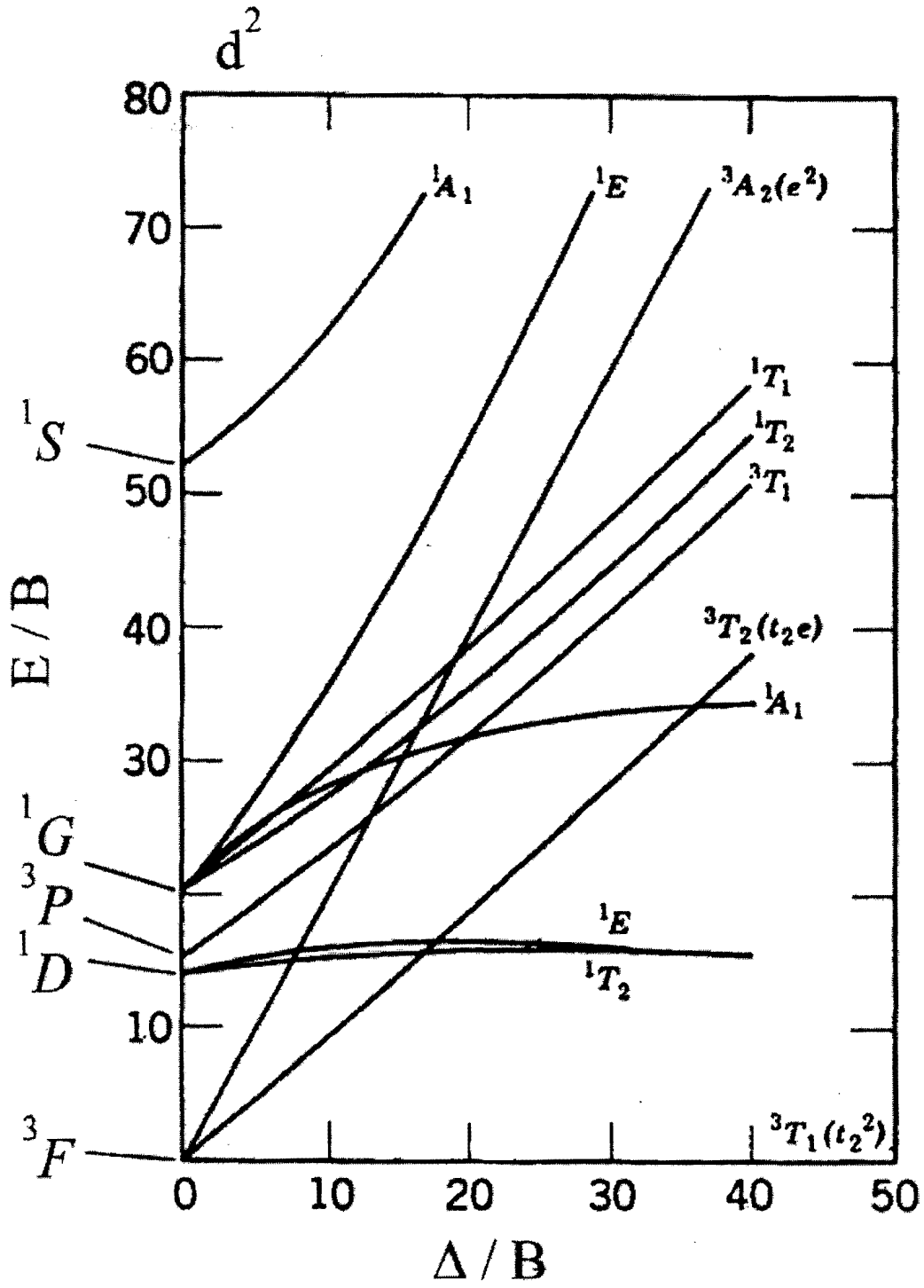
The flow-chart (Decision tree) used for assigning point groups





The 1–18 group designation has been recommended by the International Union of Pure and Applied Chemistry (IUPAC) but is not yet in wide use. In this text we use the standard U.S. notation for group numbers (1A–8A and 1B–8B). No names have been assigned for elements 112, 114, and 116. Elements 113, 115, 117, and 118 have not yet been synthesized.

C301 NOTES


d²
80
70
60
50
40
30
10
0
10
20
30
40
50
E / B
Δ / B
¹S
¹G
³P
¹D
³F
¹A₁
¹E
³A₂(e²)
¹T₁
¹T₂
³T₁
³T₂(t₂e)
¹A₁
¹E
¹T₂
³T₁(t₂²)