UNIVERSITY OF ESWATINI

MAIN EXAMINATION

ACADEMIC YEAR 2018/2019

TITLE OF PAPER:	COORDINATION AND TRANSITION METAL CHEMISTRY
COURSE NUMBER:	CHE322
TIME ALLOWED:	THREE (3) HOURS
INSTRUCTIONS:	THERE ARE FIVE (5) QUESTIONS. ANSWER ANY FOUR (4) QUESTIONS. EACH QUESTION IS WORTH 25 MARKS.

THE FOLLOWING HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER:

- Periodic Table of the Elements
- Table of Universal Constants
- Tanabe-Sugano diagrams for octahedral complexes

NON-PROGRAMMABLE ELECTRONIC CALCULATORS MAY BE USED

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

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QUESTION 1

(a) Name the following complexes

(i) $[Cr(OH_2)_6](NO_3)_3$ (ii) $K_3[Cr(C_2O_4)_3]$ (iii) $[Co(NH_3)_5(CO_3)]Cl$ [3]

(b) Determine the oxidation state for the transition metal atom or ion

(i) $[Co(py)_4]Br_2$ (ii) $[V(OH_2)_6](NO_3)_3$ (iii) $K_4[Mn(CN)_6]$ [3]

(c) Write the formula of the complexes or complex ions

(i) Tetraammineaquachloridocobalt(III) chloride

(ii) Potassium diaquatetrabromovanadate(III)

(iii)Tetrakis(trimethylphosphine)cobalt(III) sulphate

(iv) Hexaammineruthenium(III) tetrachloronickelate(II) [4]

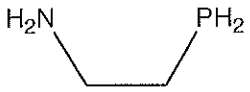
(d) State the type of isomerism that may be exhibited by the following complexes, and draw structures of the isomers:

(i) $[Cr(ox)_2(H_2O)_2]^-$ (ii) $[PdCl_2(PPh_3)_2]$ [8]

(e) Determine the overall charge, *n*, of the complexes.

(i) $[Fe^{II}(bpy)_3]^n$ (ii) $[Cr^{III}F_6]^n$ (iii) $[Co^{III}Cl_2(en)_2]^n$ [3]

(f) The (2-aminoethyl)phosphine ligand has the structure shown below; it often acts as a bidentate ligand toward transition metals. When this ligand forms monodentate complexes with palladium, it bonds through its phosphorus atom rather than its nitrogen. Suggest an explanation. [2]



(g) In the complex $[Co(NH_3)_5(H_2O)]^+$, the water molecule is replaced more readily than the ammonia ligands in a ligand substitution reaction. What can be deduced about the comparative nucleophilicity of H_2O and NH_3? [2]

QUESTION 2

(a) Explain why $[Cr(NH_3)_6]^{3+}$ is paramagnetic and $[Ni(CN)_4]^{2-}$ is diamagnetic. [8]

(b) Account for the difference in rate constants for the following two reactions:

$[Fe(H_2O)_6]^{2+} + Cl^- \longrightarrow [Fe(H_2O)_5Cl]^+ + H_2O \qquad k = 10^6\ M^{-1}s^{-1}$

$[Ru(H_2O)_6]^{2+} + Cl^- \longrightarrow [Ru(H_2O)_5Cl]^+ + H_2O \qquad k = 10^{-2}\ M^{-1}s^{-1}$ [6]

(c) The rate of attack on Co(III) by an entering ligand Y is independent of Y with the spectacular exception of the rapid reaction with OH^-. Explain the anomaly. [5]

(d) Assign an outer and inner sphere mechanism for the following:

(i) The rate of reduction of $[Co(NH_3)_5Py]^{3+}$ by $[Fe(CN)_6]^{4-}$ are insensitive to substitution by Py. [3]

(ii) The intermediate $[Fe(NCS)(OH_2)_5]^{2+}$ can be detected in the reaction of $[Co(NCS)(NH_3)_5]^{2+}$ with $Fe^{2+}(aq)$ to give $Fe^{3+}(aq)$ and $Co^{2+}(aq)$ [3]

QUESTION 3

(a) For each of the following complexes, give the oxidation state of the metal and its d^n configuration:

(i) $[FeCl_4]^{2-}$ (ii) $[Ti(H_2O)_6]^{3+}$ (iii) $[Cr(acac)_3]$ [6]

(b) For which member of the following pairs would Δ_o be larger and why:

(i) $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$

(ii) $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$

(iii) $[Co(en)_3]^{3+}$ and $[Rh(en)_3]^{3+}$ [6]

(c) Suggest products A and B in the following ligand substitution reaction:

$$[PtCl_4]^{2-} \xrightarrow{NH_3} \mathbf{A} \xrightarrow{NH_3} \mathbf{B}$$ [2]

(d) The following data have been obtained at 50°C for the aquation of $[Cr(NH_3)_5X]^{2+}$ (k_{aq}) and the anation by Y^- of $[Cr(NH_3)_5(H_2O)]^{3+}$ (k_{an}).

Y^-	$k_{aq}(M^{-1}sec^{-1})$	$k_{an}(M^{-1}sec^{-1})$
NCS^-	0.11×10^{-4}	4.16×10^{-5}
$CCl_2CO_2^-$	0.37×10^{-4}	1.81×10^{-5}
Cl^-	1.75×10^{-4}	0.69×10^{-4}
Br^-	12.5×10^{-4}	2.47×10^{-4}
I^-	102×10^{-4}	6.45×10^{-4}

What can you say about the mechanism of these reactions? [4]

(e) Name and draw structures of octahedral complex ions

(i) *cis*-$[CrCl_2(NH_3)_4]^+$

(ii) *trans*-$[Cr(NCS)_4(NH_3)_2]^-$

(iii) $[Co(C_2O_4)(en)_2]^+$

Is the oxalate complex *cis* or *trans*?

[7]

QUESTION 4

(a) How does each of the following modifications affect the rate of a square planar complex substitution reaction?

(i) Changing a trans ligand from H to Cl

(ii) Changing the leaving group from Cl to I

(iii) Adding a bulky substituent on a *cis* ligand

(iv) Increasing the positive charge on the complex

[8]

(b) Discuss evidence for dissociative mechanism in acid hydrolysis. [9]

(c) Put the following complexes in increasing order of rate of substitution by H_2O and briefly explain your reasoning.

$[Co(NH_3)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$, $[Ir(NH_3)_6]^{3-}$, $[Mn(OH_2)_6]^{2+}$, $[Ni(OH_2)_6]^{2+}$ [8]

QUESTION 5

(a) The most intense absorption band in the visible spectrum of $[Mn(H_2O)_6]^{2+}$ is at 24,900 cm^{-1} and has a molar absorptivity of 0.038 L mol^{-1} cm^{-1}.

(i) What concentration of $[Mn(H_2O)_6]^{2+}$ would be necessary to give an absorbance of 0.10 in a cell of path length 1.00 cm?

(ii) Determine the wavelength and frequency of 24,900 cm^{-1} light.

(iii) Determine the energy and frequency of 366 nm light. [9]

(b) A 2.00 x 10^{-4} M solution of $Fe(S_2CNEt_2)_3$ (Et = C_2H_5) in $CHCl_3$ at 25° C has absorption bands at 350 nm (A = 2.34), 514 nm (A = 0.532), 590 nm (A = 0.370), and 1540 nm (A = 0.0016).

(i) Calculate the molar absorptivity for this compound at each wavelength.

(ii) Are these bands more likely due to d–d transitions or charge-transfer transitions? Explain. [8]

(c) Predict the relative positions of the absorption maximum in the spectra of $[Ti(CN)_6]^{3-}$, $[TiCl_6]^{3-}$ and $[Ti(H_2O)_6]^{3+}$ [6]

(d) What is the crystal field stabilization energy (CFSE) for octahedral ions of the following configurations? [2]

(i) d^9 (ii) d^5

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	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	28.086 **Si** 14	30.974 **P** 15	32.06 **S** 16	35.453 **Cl** 17	39.948 **Ar** 18
4	39.098 **K** 19	40.078 **Ca** 20	44.956 **Sc** 21	47.88 **Ti** 22	50.942 **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	92.906 **Nb** 41	95.94 **Mo** 42	98.907 **Tc** 43	101.07 **Ru** 44	102.91 **Rh** 45	106.42 **Pd** 46	107.87 **Ag** 47	112.41 **Cd** 48	114.82 **In** 49	118.71 **Sn** 50	121.75 **Sb** 51	127.60 **Te** 52	126.90 **I** 53	131.29 **Xe** 54
6	132.91 **Cs** 55	137.33 **Ba** 56	138.91 ***La** 57	178.49 **Hf** 72	180.95 **Ta** 73	183.85 **W** 74	186.21 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.97 **Au** 79	200.59 **Hg** 80	204.38 **Tl** 81	207.2 **Pb** 82	208.98 **Bi** 83	(209) **Po** 84	(210) **At** 85	(222) **Rn** 86
7	223 **Fr** 87	226.03 **Ra** 88	(227) ****Ac** 89	(261) **Rf** 104	(262) **Ha** 105	(263) **Unh** 106	(262) **Uns** 107	(265) **Uno** 108	(266) **Une** 109	(267) **Uun** 110								

Atomic mass → 10.811
Symbol → **B**
Atomic No. → 5

TRANSITION ELEMENTS

*Lanthanide Series	140.12 **Ce** 58	140.91 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.96 **Eu** 63	157.25 **Gd** 64	158.93 **Tb** 65	162.50 **Dy** 66	164.93 **Ho** 67	167.26 **Er** 68	168.93 **Tm** 69	173.04 **Yb** 70	174.97 **Lu** 71
**Actinide Series	232.04 **Th** 90	231.04 **Pa** 91	238.03 **U** 92	237.05 **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

( ) indicates the mass number of the isotope with the longest half-life.

General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\ 924\ 58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\ 177 \times 10^{-19}$ C
Faraday constant	$F = N_A e$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\ 66 \times 10^{23}$ J K^{-1}
Gas constant	$R = N_A k$	$8.314\ 51$ J K^{-1} mol^{-1}
		$8.205\ 78 \times 10^{-2}$ dm^3 atm K^{-1} mol^{-1}
		6.2364×10 L Torr 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		
electron	m_e	$9.109\ 39 \times 10^{-31}$ Kg
proton	m_p	$1.672\ 62 \times 10^{-27}$ Kg
neutron	m_n	$1.674\ 93 \times 10^{-27}$ Kg
Vacuum permittivity	$\varepsilon_o = 1/c^2\mu_o$	$8.854\ 19 \times 10^{-12}$ J^{-1} C^2 m^{-1}
	$4\pi\varepsilon_o$	$1.112\ 65 \times 10^{-10}$ J^{-1} C^2 m^{-1}
Vacuum permeability	μ_o	$4\pi \times 10^{-7}$ J s^2 C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^2 J^{-1} C^{-2} m^3
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\ 02 \times 10^{-24}$ J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\ 79 \times 10^{-27}$ J T^{-1}
g value	g_e	$2.002\ 32$
Bohr radius	$a_o = 4\pi\varepsilon_o\hbar/m_e e^2$	$5.291\ 77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_o e^2 c/2h$	$7.297\ 35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_o^2$	$1.097\ 37 \times 10^{7}$ m^{-1}
Standard acceleration of free fall	g	$9.806\ 65$ m s^{-2}
Gravitational constant	G	$6.672\ 59 \times 10^{-11}$ N m^2 Kg^{-2}

Conversion factors

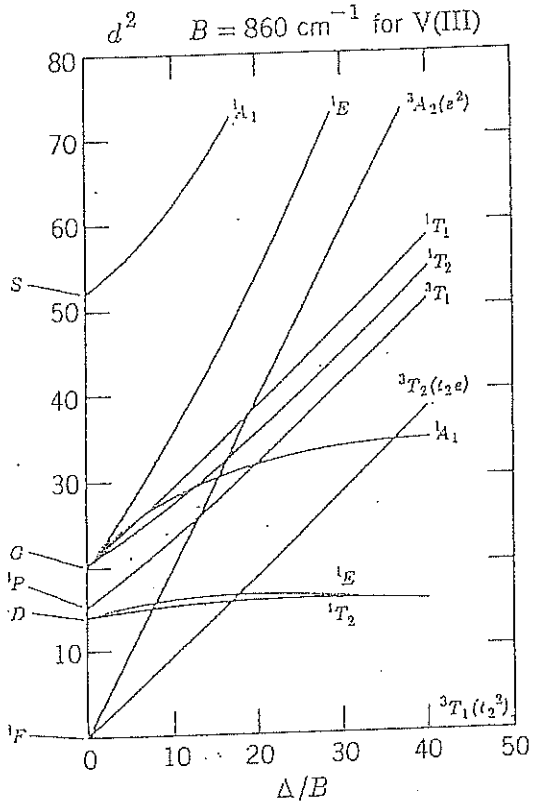
1 cal	4.184 joules (J)	1 erg	1×10^{-7} J
1 eV	$1.602\ 2 \times 10^{-19}$ J	1 eV/molecule	96 485 kJ mol^{-1}
			23.061 kcal mol^{-1}

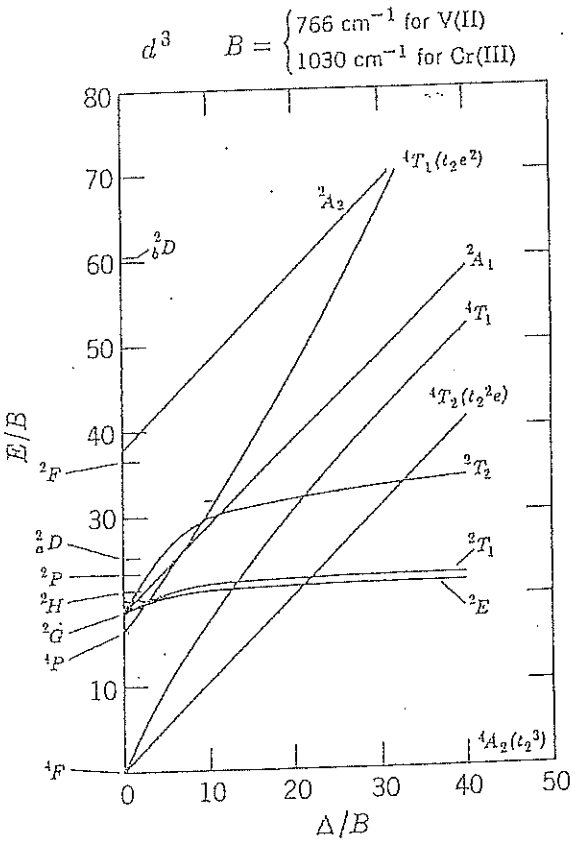
f	p	n	μ	m	c	d	k	M	G	**Prefixes**
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga	
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}	

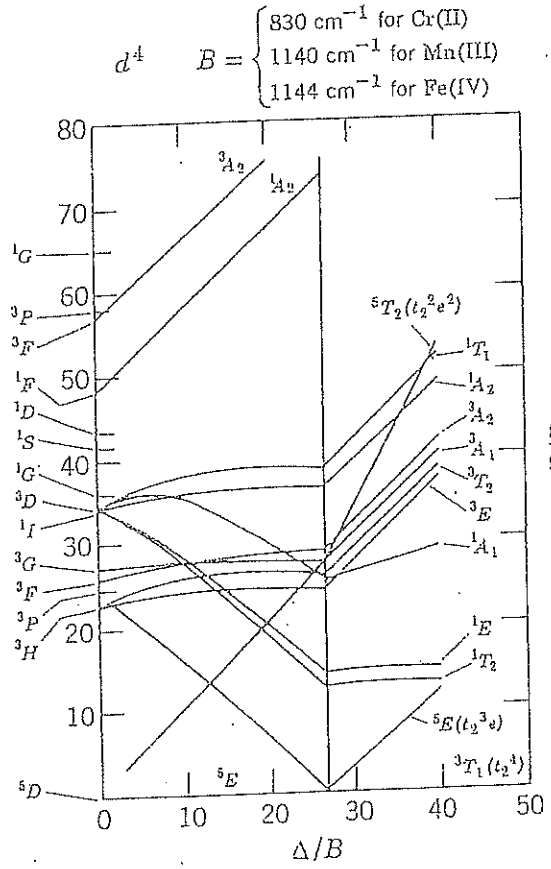
Spectrochemical Series

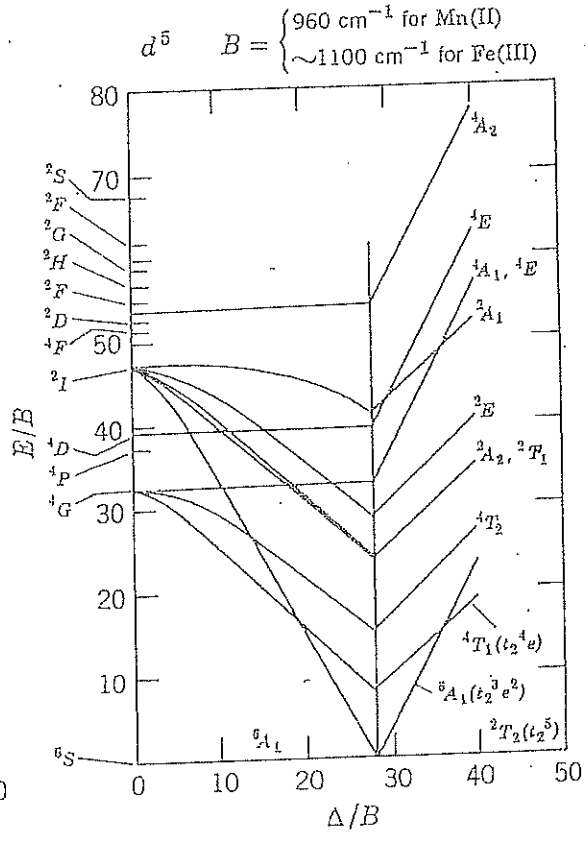
$I^- < Br^- < S^{2-} < Cl^- < NO_3^- < F^- < OH^- < EtOH < C_2O_4^{2-} < H_2O < EDTA < (NH_3, py) <$ en < dipy $< NO_2^- < CN^- < CO$.

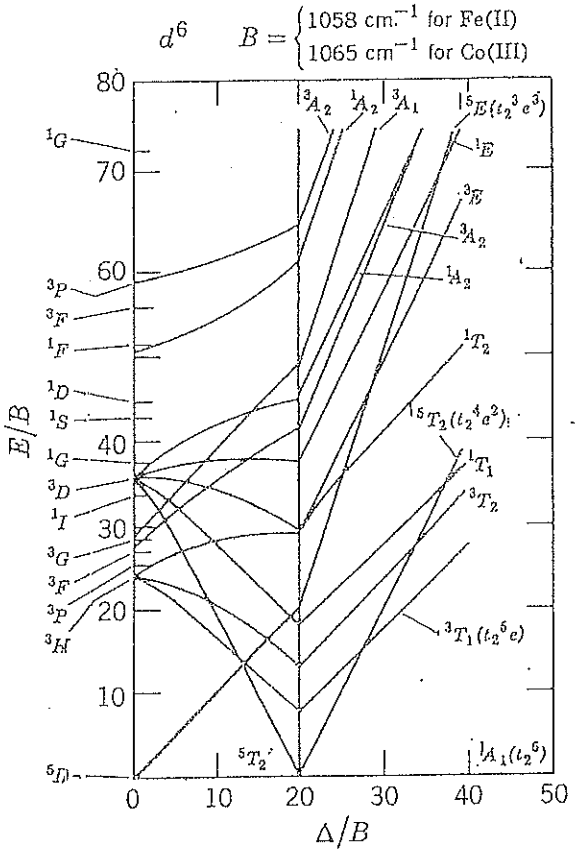
Tanabe and Sugano Diagram

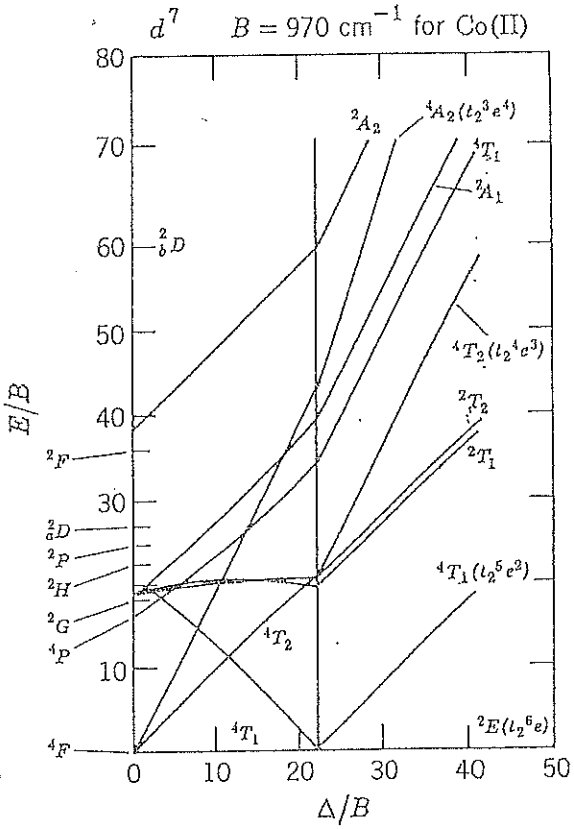


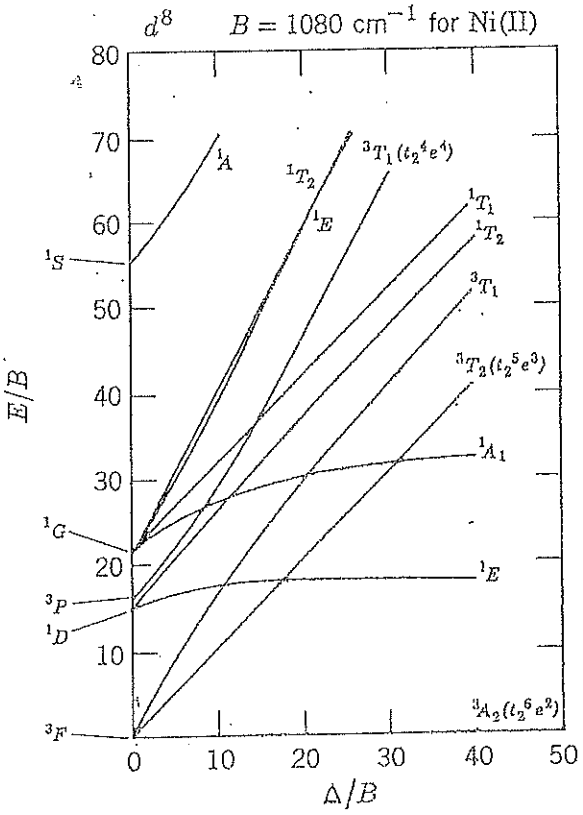







d^6
$B = \begin{cases} 1058\ \text{cm}^{-1}\ \text{for Fe(II)} \\ 1065\ \text{cm}^{-1}\ \text{for Co(III)} \end{cases}$
E/B
Δ/B
$^5T_2$
$^1A_1(t_2^6)$
$^3T_1(t_2^5e)$
$^5T_2(t_2^4e^2)$
$^5E(t_2^3e^3)$


d^7
$B = 970\ \text{cm}^{-1}$ for Co(II)
E/B
Δ/B
$^4T_1$
$^2E(t_2^6e)$
$^4T_1(t_2^5e^2)$
$^4T_2(t_2^4e^3)$
$^4A_2(t_2^3e^4)$


d^8
$B = 1080\ \text{cm}^{-1}$ for Ni(II)
E/B
Δ/B
$^3A_2(t_2^6e^2)$
$^3T_2(t_2^5e^3)$
$^3T_1(t_2^4e^4)$