FACULTY OF SCIENCE

Department of Chemistry

MODULE:	**CEM3A20**
	Coordination Chemistry
CAMPUS:	APK
TEST:	**Supp. Examination**
DATE:	July 2019
SESSION:	15:00–17:00
ASSESSOR:	Dr B.C.E Makhubela
EXTERNAL MODERATOR:	Prof HS Clayton (Unisa)
DURATION:	3 hours
MARKS:	100

QUESTION 1 **[14]**

1.1 Using Hard and Soft Acid and Base Principles (HSAB) predict which direction, forward or reverse, the following reactions will proceed and explain why.

a) $2CH_3MgF + HgF_2 \rightleftharpoons (CH_3)_2Hg + 2MgF_2$ [2]

b) $CdSe + HgS \rightleftharpoons CdS + HgSe$ [2]

1.2 Arrange the following ions in order of increasing Brønsted acidity and account for this trend. $[Al(OH_2)_6]^{3+}$,$[Fe(OH_2)_6]^{3+}$ and $[Fe(OH_2)_6]^{2+}$ [3]

1.3 Which is the stronger base between PH_3 and PF_3? Give an explanation for your answer. [3]

1.4 Use Drago-Wayland E and C parameters to calculate Δ*H* for the reactions of BF_3 and $B(CH_3)_3$ and diethyl sulphide $(C_2H_5)_2S$. Give two reasons for the difference in reactivity. [4]

QUESTION 2 **[19]**

2.1 Draw the structures of all possible stereoisomers of the octahedral complex $[Fe(en)(ox)Br_2]^-$ and the square planar complex $[Pd(PPh_3)_2BrCl]$. [5]

2.2 Write the structural formula for the isomers of $[Co(NH_3)_5(ONO)]Cl$ and $[Co(o\text{-phen})_2(NH_3)(SCN)]Cl$. In each case, specify which kind of isomerism is exhibited. [4]

2.3 Give the IUPAC name for $[Cr(NH_3)_4(OH)_2]Br$ [2]

2.4 What is the electron configuration, coordination number, geometry and oxidation state of Ni in $[NiCl_4]^{2-}$? [4]

2.5 Draw the structure of the $[Fe(ox)_3]^{3-}$ complex ion, give the denticity of the ligand and state how many chelate rings this complex ion contains. [4]

QUESTION 3 **[22]**

3.1 When the d-orbitals of a transition metal ion are split in energy (in an octahedral ligand field) which orbitals are raised least in energy? [3]

3.2 What are the factors that lead to an increase in the magnitude of Δo in coordination compounds? [4]

3.3 The complex ion $[Co(CO_3)_3]^{3-}$, is an octahedral complex with bidentate carbonate ions (CO_3^{2-}) as ligands, has one absorption band in the visible region of the UV-visible spectrum at 700 nm.

a) Predict the colour of this complex, and explain your reasoning. [2]

b) Is the carbonate ion a weak- or strong-field ligand? Explain. [2]

c) Give the d-orbital electron configuration and predict how many unpaired electrons are present in $[Co(CO_3)_3]^{3-}$. Further deduce whether the complex is paramagnetic or diamagnetic. [4]

d) Calculate the Crystal Field Stabilization Energy (CFSE) of $[Co(CO_3)_3]^{3-}$ in units of Δ_o and the magnetic moment. [3]

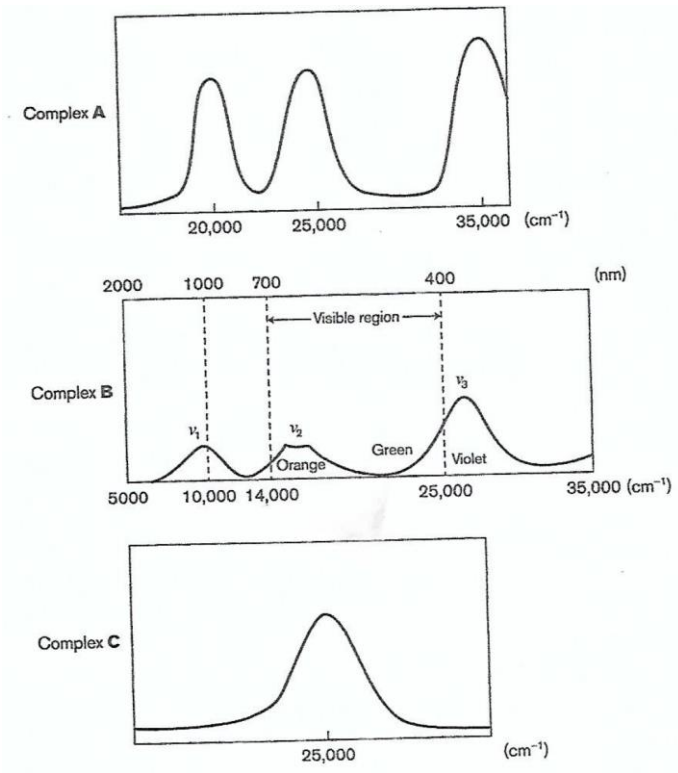
3.4 Which of the following is the stronger acid? Which has the higher Δ_o? Briefly rationalize your choices. [4]

$[Ru(H_2O)_6]^{2+}$ and $[Ru(H_2O)_6]^{3+}$

QUESTION 4 **[17]**

4.1 Calculate the ground state spectroscopic term symbol for a d^2 free ion. Show all your calculations. [3]

4.2 The absorption spectra shown below are of three octahedral complexes **A**, **B** and **C**.



a) Which spectrum is more likely to be that of a d^1 metal ion and why? [2]

b) Is the colour of complex **B**, orange, green or violet? Explain [2]

c) What is the approximate value of Δ_o for complex **B**? [1]

d) Which complex has the highest value of Δ_o? [1]

4.2 Bushveld minerals, a South African mining company, found a magnetite layer from which they isolated an unknown transition metal ion with one d electron. This metal electron absorbs light with a wavelength of 640 nm, and the absorption band has a molar absorptivity (ε) of 8.

a) Is this absorption a charge transfer (CT) or a d-d transition absorption band? Explain.

b) What colour of light was absorbed and what colour will a solution of this ion have? [2]

c) Will the colour be intense, of moderate intensity or weak? Explain [2]

d) What is the energy of this absorption in cm^{-1}? [2]

e) From the following transition metal ions, which one is likely the unknown metal ion: Cr^{3+},V^{4+}, Fe^{3+}. Why? [2]

QUESTION 5 **[15]**

5.1 For $[Pd(CN)_4]^{2-}$ a value of log β_4 of 62.3 has been determined. To what equilibrium process does this value refer? [3]

5.2 Arrange the following metal ions in order of increasing stability with oxalic acid and explain your answer. [3]

Cu^{2+}, Mn^{2+}, Fe^{2+} and Ni^{2+}

5.2 Explain the macrocyclic effect with the aid of an example? In your answer also explain which thermodynamic term(s) drive this effect? [9]

QUESTION 6 **[13]**

6.1 Design a selective two-step synthesis for *cis*- and *trans*-$[Pt(NH_3)(PMe_3)Cl_2]$ starting with $[PtCl_4]^{2-}$. Briefly explain your chosen synthetic procedure. [8]

6.2 Shown below is a two-step dissociative mechanism process for the substitution of a ligand X with Y in an octahedral complex.

$$[ML_5X] + Y \rightleftharpoons [ML_5] + X$$

$$[ML_5] + Y \longrightarrow [ML_5Y] + X$$

a) If the rate-determining step is addition of the entering ligand Y to the intermediate, $[ML_5]$, draw a reaction profile (reaction energy diagram) for this process. [4]

b) If the rate of substitution is dependent on the nature of the incoming ligand, Y, how would you denote the mechanism of this reaction? [1]

End of paper – Total marks = 100

Supplementary information starts on the next page

Useful Equations and Supplementary Information

$pH = pK_a – (1/n) \log[M^{n+}] – 5.6/n$

Pauling's OpE(OH)q, $pK_a \approx 9 – 7p$.

Bell's rule : OpE(OH)q, $pK_a \approx 8 – 5p$.

Spin-only formula: $\mu_s = 2\{S(S+1)\}1/2$ BM = $\{n(n+2)\}1/2$ BM

$-\Delta H = E_A E_B + C_A C_B$

$\Delta G^o = \Delta H^o - T\Delta S^o$ and $\Delta G^o = -RT \ln K$

$R = 8.314\ JK^{-1}mol^{-1}$

Planck's constant (h) = 6.62661×10^{-34} Js

Speed of light (c) = 2.9970×10^8 m/s

Avogadro's number = 6.02214×10^{23} molecules/mol

Drago's C_A, E_A, C_B, and E_B values

TABLE 6.8 C_A, E_A, C_B, and E_B Values (kcal/mol)

Acid	C_A	E_A
Trimethylboron, $B(CH_3)_3$	1.70	6.14
Boron trifluoride (gas), BF_3	1.62	9.88
Trimethylaluminum, $Al(CH_3)_3$	1.43	16.9
Iodine (standard), I_2	1.00*	1.00*
Trimethylgallium, $Ga(CH_3)_3$	0.881	13.3
Iodine monochloride, ICl	0.830	5.10
Sulfur dioxide, SO_2	0.808	0.920
Phenol, C_6H_5OH	0.442	4.33
tert-butyl alcohol, C_4H_9OH	0.300	2.04
Pyrrole, C_4H_4NH	0.295	2.54
Chloroform, $CHCl_3$	0.159	3.02
Base	C_B	E_B
1-Azabicyclo[2.2.2] octane,		
Quinuclidine, $HC(C_2H_4)_3N$	13.2	0.704
Trimethylamine, $(CH_3)_3N$	11.54	0.808
Triethylamine, $(C_2H_5)_3N$	11.09	0.991
Dimethylamine, $(CH_3)_2NH$	8.73	1.09
Diethyl sulfide, $(C_2H_5)_2S$	7.40*	0.399
Pyridine, C_5H_5N	6.40	1.17
Methylamine, CH_3NH_2	5.88	1.30
Ammonia, NH_3	3.46	1.36
Diethyl ether, $(C_2H_5)_2O$	3.25	0.963
N,N-dimethylacetamide, $(CH_3)_2NCOCH_3$	2.58	1.32*
Benzene, C_6H_6	0.681	0.525

NOTE: *Reference values.

Source: Data from R. S. Drago, *J. Chem. Educ.*, **1974**, *51*, 300.

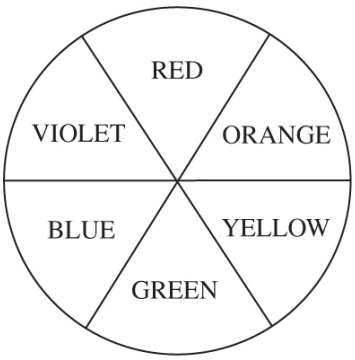
The Spectrochemical Series

$CO, CN^- > PPh_3 > phen > NO_2^- > en > NH_3 > NCS^- > H_2O > F^- > RCO_2^- > OH^- > C\ell^- > Br^- > I^-$

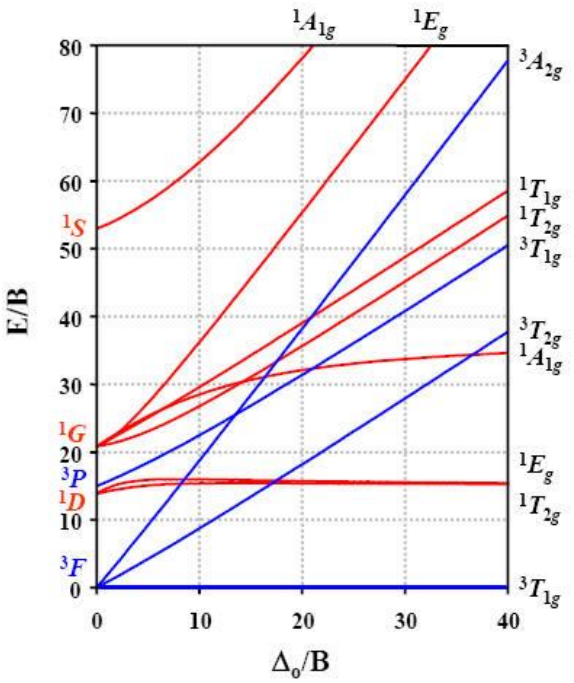
Strong field, low spin π-acceptor	σ-donor only	Weak field, high spin π-donor

Table and colour wheel of visible light and their complimentary colours

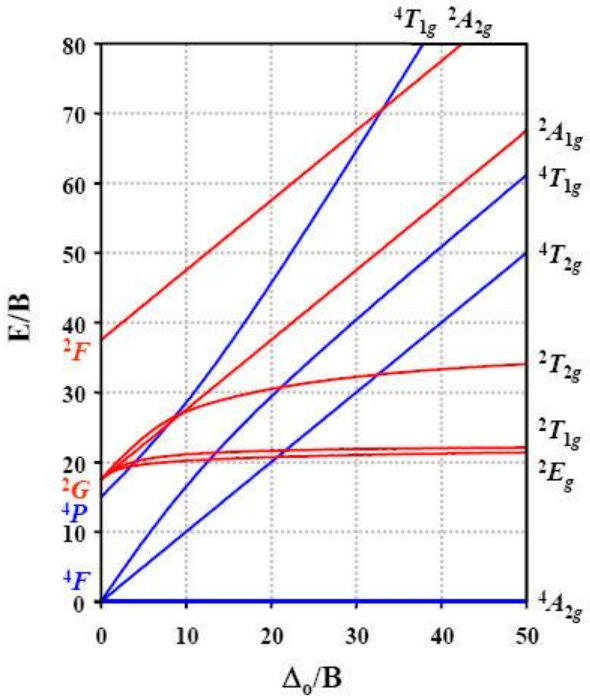
Wavelength Range (nm)	Wave Numbers (cm^{-1})	Color	Complementary Color
< 400	> 25,000	Ultraviolet	
400–450	22,000–25,000	Violet	Yellow
450–490	20,000–22,000	Blue	Orange
490–550	18,000–20,000	Green	Red
550–580	17,000–18,000	Yellow	Violet
580–650	15,000–17,000	Orange	Blue
650–700	14,000–15,000	Red	Green
> 700	< 14,000	Infrared	



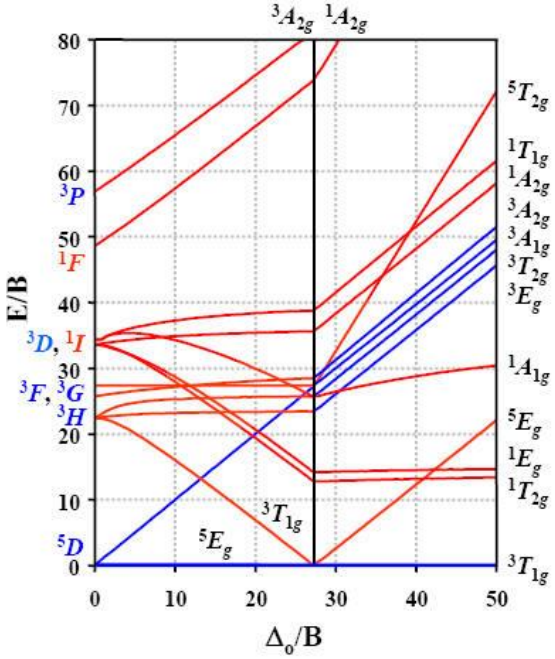
d^2 Tanabe-Sugano Diagram



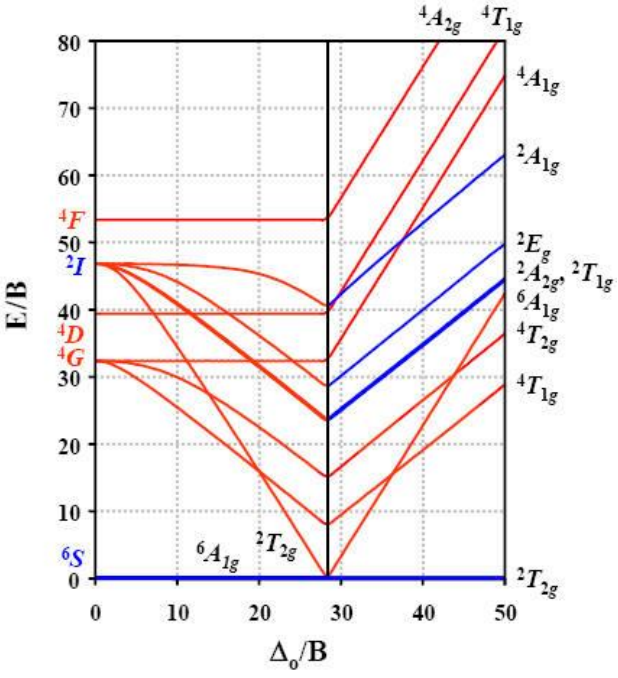
d^3 Tanabe-Sugano Diagram



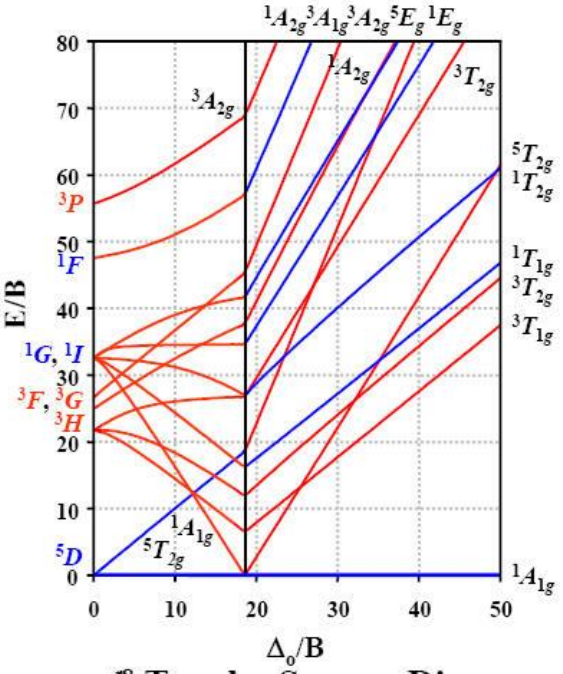
d^4 Tanabe-Sugano Diagram



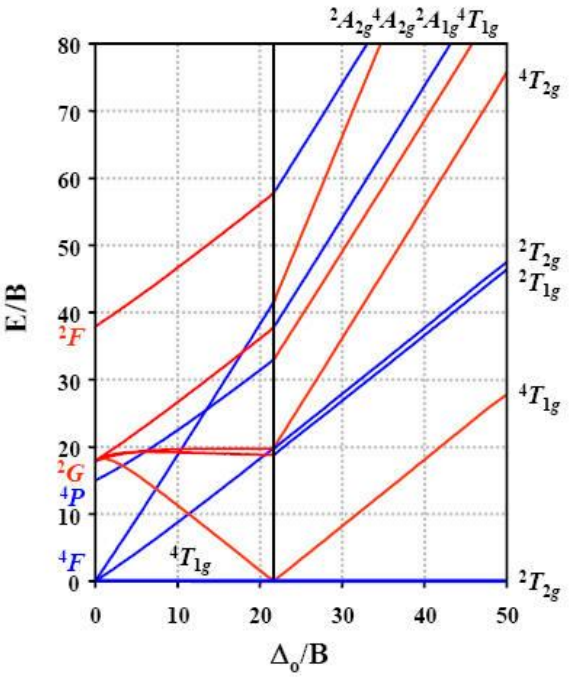
d^5 Tanabe-Sugano Diagram



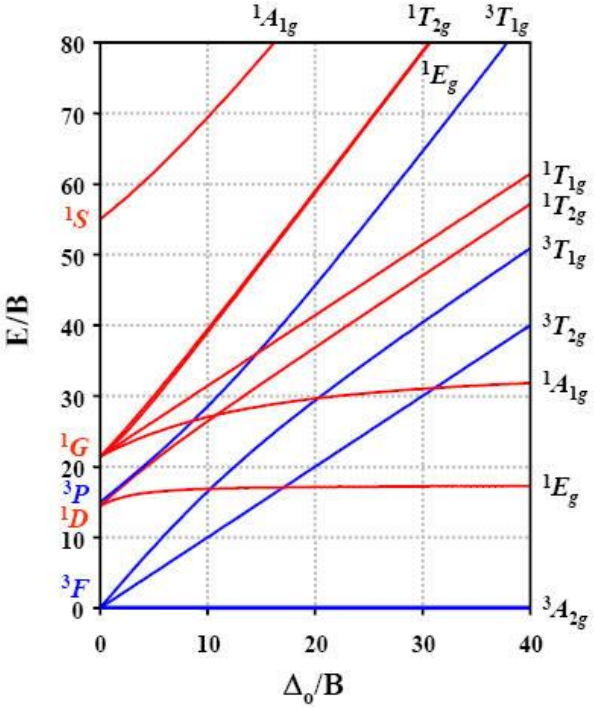
d^6 Tanabe-Sugano Diagram

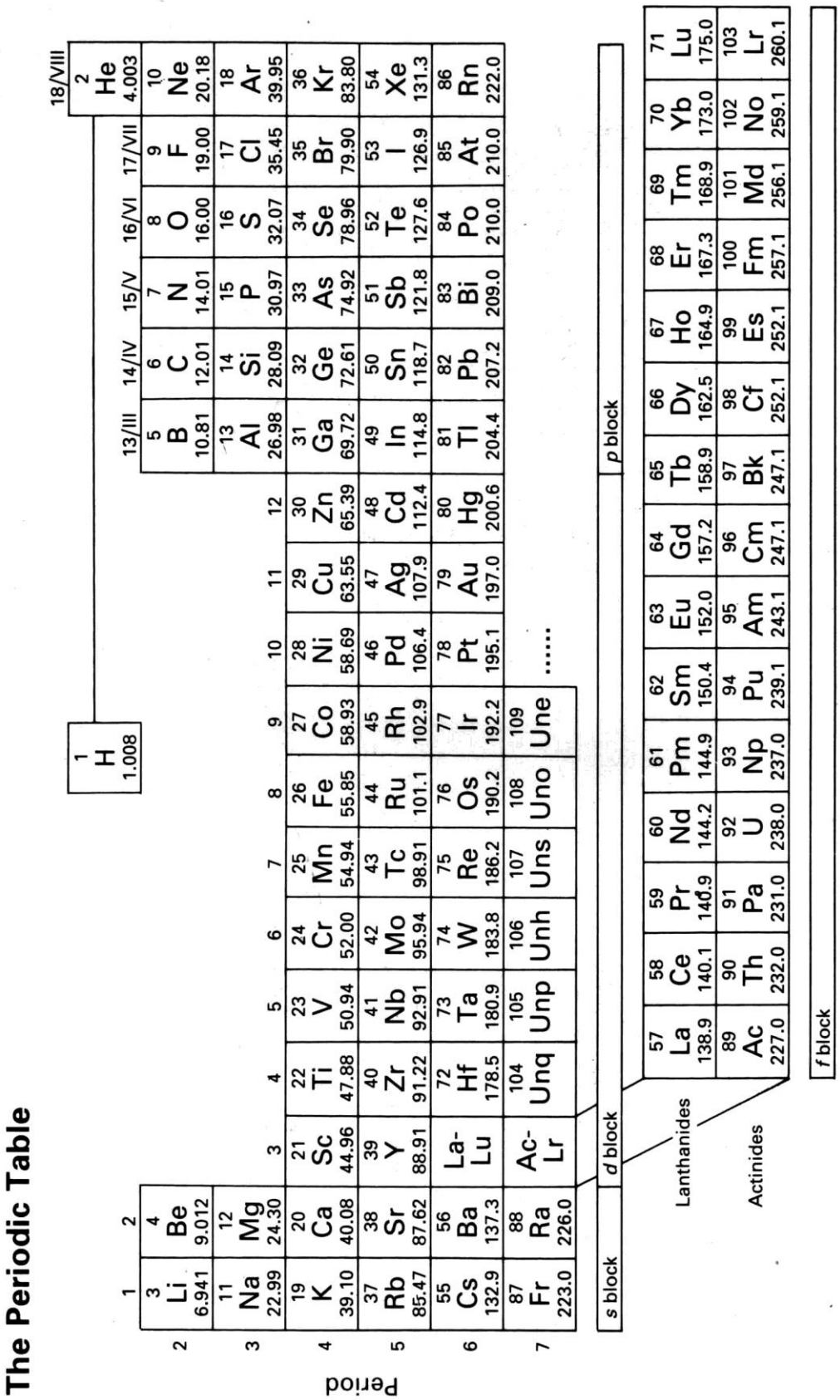


d^7 Tanabe-Sugano Diagram



d^8 Tanabe-Sugano Diagram




The Periodic Table
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Actinides
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d block
p block
f block
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2 He 4.003
3 Li 6.941
4 Be 9.012
5 B 10.81
6 C 12.01
7 N 14.01
8 O 16.00
9 F 19.00
10 Ne 20.18
11 Na 22.99
12 Mg 24.30
13 Al 26.98
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15 P 30.97
16 S 32.07
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18 Ar 39.95
19 K 39.10
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24 Cr 52.00
25 Mn 54.94
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28 Ni 58.69
29 Cu 63.55
30 Zn 65.39
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32 Ge 72.61
33 As 74.92
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35 Br 79.90
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37 Rb 85.47
38 Sr 87.62
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40 Zr 91.22
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Ac- Lr
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84 Po 210.0
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86 Rn 222.0
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105 Unp
106 Unh
107 Uns
108 Uno
109 Une
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