QUESTION 1 [11]

1.1. Define an oxo acid and give an example of one such acid.

[2]

1.2. Distinguish between an Interchange and dissociative mechanism for substitution on metal ions.

[4]

1.3. Define the trans-effect.

[2]

1.4. How can an inner sphere redox reaction be distinguished from an outer sphere redox reaction?

[3]

QUESTION 2 [20]

2.1. For the following complexes, give the systematic (IUPAC) names, and indicate the electron configuration of the metal ion and give the geometry (shape) of the complex

(a) *trans*-$[Co(en)_2I(H_2O)](NO_3)_2$

(b) $[Co(NH_3)_5]\text{-}NH_2\text{-}[Co(NH_3)_4(H_2O)]Cl_5$ [8]

2.2. Write the structural formula for the following complexes:

(a) diamminesilver(I) dicyanoargentate(I)

(b) Tetrahydroxozincate(II)

[4]

2.3. Identify the types of isomerism and write the formulas that are possible for the complexes with the following molecular formulas:

(a) $[Pt(PEt_3)_3(SCN)]$

(b) $[CoBr(NH_3)_5](SO_4)$

(c) $[FeCl_2]\text{-}6H_2O$

[6]

2.4. What are monodentate and bidentate ligands? [2]

QUESTION 3 [16]

3.1. List four factors that affect the magnitude of crystal field splitting [4]

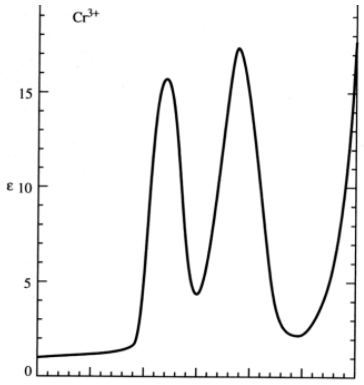
3.2. Explain in detail how the d orbital splitting pattern of tetrahedral metal complexes are formed by evaluating the geometry of the relevant d orbitals in a tetrahedral ligand field in detail. [6]

3.3. Determine the number of unpaired electrons, magnetic spin only moment, and the crystal field stabilization energy as a multiple of Δ_o for $[Fe(H_2O)_6]^{3+}$ complex ion. [6]

QUESTION 4 [15]

4.1. Describe the Jahn-Teller effect in detail, using a d^9 species like Cu(II). [5]

4.2. The electronic spectrum below is that of a Cr^{3+} metal complex and the absorption peaks are 8 600 cm^{-1}, 13 600 cm^{-1} and 23 200 cm^{-1}.



(a) Using the appropriate Tanabe-Sugano diagram, Identify the predicted spectral bands. [3]

(b) calculate Δ_O and the Racah parameter (*B)* for this complex ion. [7]

QUESTION 5 [9]

5.1. Explain the macrocyclic effect with the aid of an example? [5]

5.2. Place the following ligands in order of increasing stability with Cu^{2+} and explain your answer. [4]

QUESTION 6 [21]

6.1 Using the principles of HSAB theory determine, giving reason, whether $K_{eq} > 1$ or $K_{eq} < 1$ for:

[2]

$$NH_2^-(aq) + H_2O(l) \leftrightarrow NH_3(aq) + OH^-(aq)$$

6.2 Which is the stronger acid in water between $[Ru(H_2O)_6]^{2+}$ and $[Ru(H_2O)_6]^{3+}$? briefly explain why?

[2]

6.2. What type of acid do we refer to $[Ru(H_2O)_6]^{3+}$ as? Give a chemical equation that shows how $[Ru(H_2O)_6]^{3+}$ acts as an acid.

[3]

6.2 Using Drago-Wayland E, C parameters, determine which of Et_3N, Et_2O and PMe_3 is the stronger base toward $GaMe_3$.

[8]

6.3 Which metal ion is a stronger Lewis acid between Li^+ and Be^{2+}, explain your choice.

[2]

6.3 Although in the gas phase, the following amine bases exhibit the trend:

$NMe_3 > NHMe_2 > NH_2Me > NH_3$ in base strength:

In aqueous solution, the trend is: $NHEt_2 > NH_2Et \sim NEt_3 > NH_3$. Briefly explain this observed difference in base strength in the aqueous solution. [2]

Is OH^- or S^{2-} more likely to form an insoluble salt with a +3 transition metal ion? Explain.

[2]

QUESTION 7 [8]

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

[4]

7.2 Suggest, giving reasons, which redox mechanism is operating in the following reactions.

[4]

(a) $[Cr^*(H_2O)_5Cl]^{3+} + [Cr(H_2O)_6]^{2+} \rightarrow [Cr(H_2O)_6]^{3+} + [Cr^*(H_2O)_5Cl]^{2+}$ $k = 0.02\ M^{-1}s^{-1}$

(b) $[Cr^*(H_2O)_5Br]^{3+} + [Cr(H_2O)_6]^{2+} \rightarrow [Cr(H_2O)_6]^{3+} + [Cr^*(H_2O)_5Br]^{2+}$ $k = 9.0\ M^{-1}s^{-1}$

End of paper – Total marks = 100

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

The Spectrochemical Series

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

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

Order in nucleophilicity of typical Lewis bases

$CN^-, CO < PR_3 < H^- < I^- < Br^- < Cl^- < H_2O$

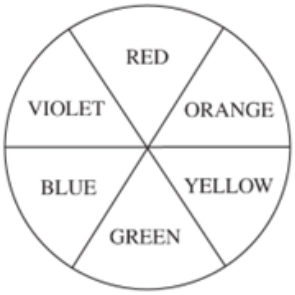
Trans- directing abilities

$R_3Si^- = R^- = H^- > PEt_3 > PMe_2Ph > PPh_3 > P(OPh)_3 = CN^- > SEt_2 >$

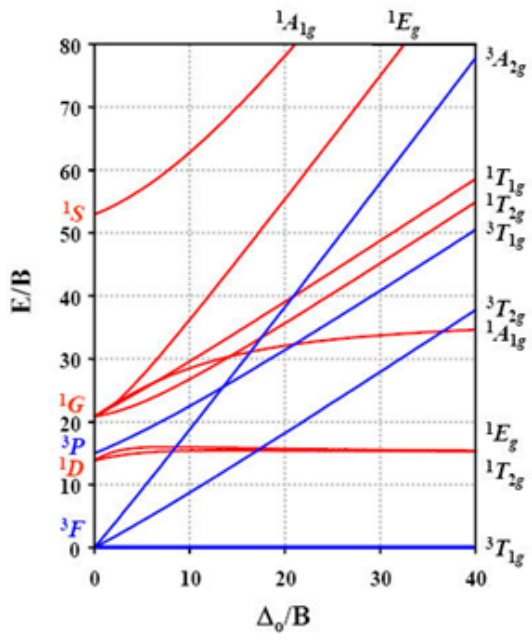
$Et_2NH > py > OSMe_2 = C_2H_4 = CO > Cl^-$

Table and colour wheel of visible light and their complimentary colours

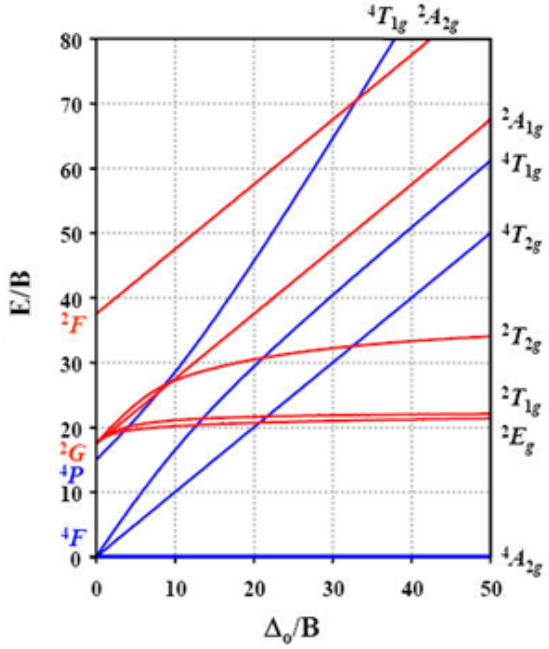
Wavelength Range (nm)	Wave Numbers (cm^{-1})	Color	Complementary Color
< 400	> 25,000	Ultraviolet	
400–450	22,000–25,000	Violet	Yellow
450–490	20,000–22,000	Blue	Orange
490–550	18,000–20,000	Green	Red
550–580	17,000–18,000	Yellow	Violet
580–650	15,000–17,000	Orange	Blue
650–700	14,000–15,000	Red	Green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



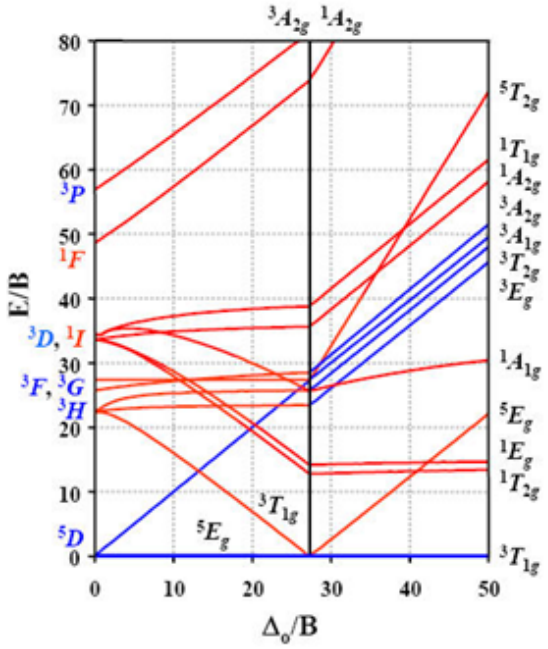
d^2 Tanabe-Sugano Diagram



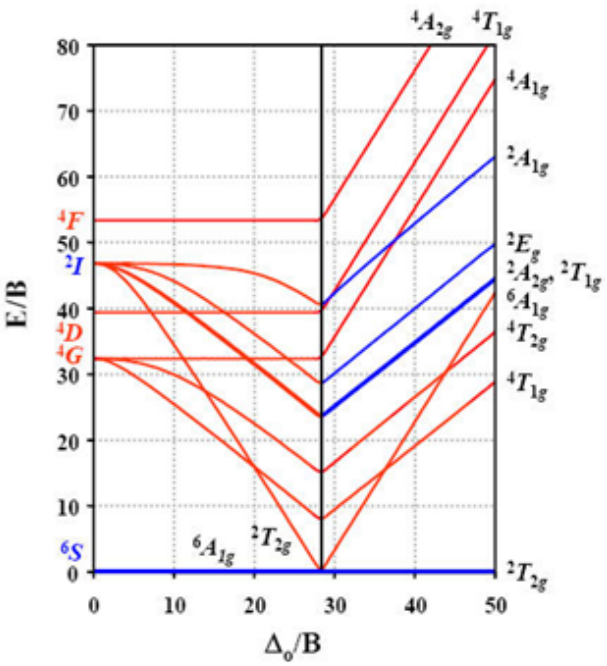
d^3 Tanabe-Sugano Diagram



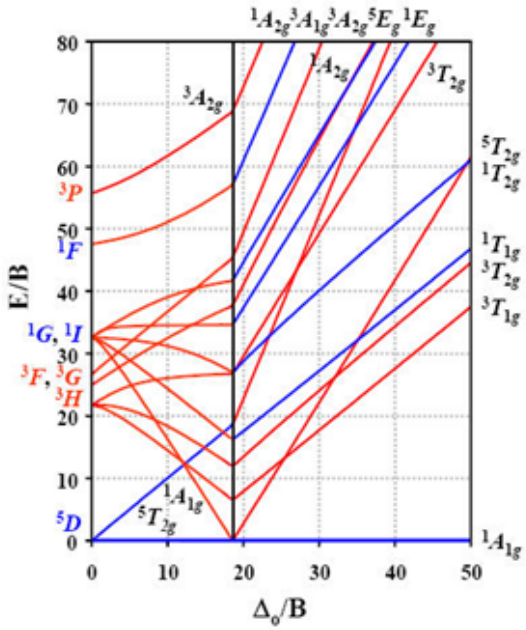
d^4 Tanabe-Sugano Diagram



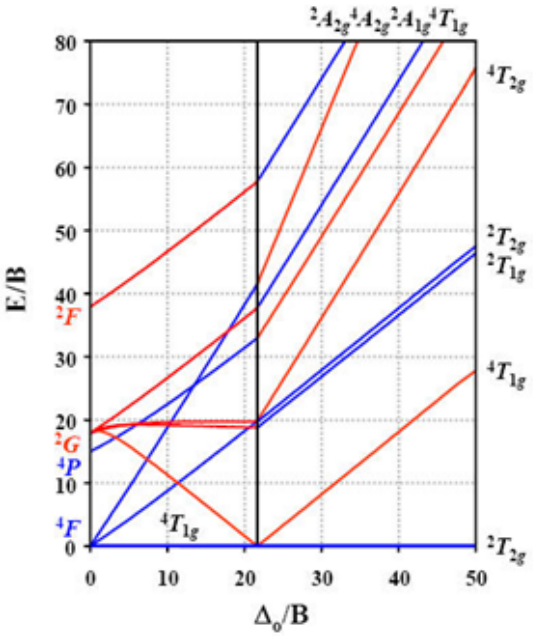
d^5 Tanabe-Sugano Diagram



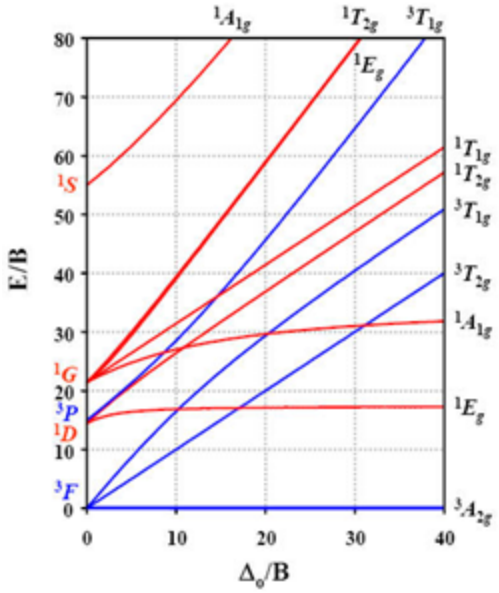
d^6 Tanabe-Sugano Diagram



d^7 Tanabe-Sugano Diagram



d^8 Tanabe-Sugano Diagram



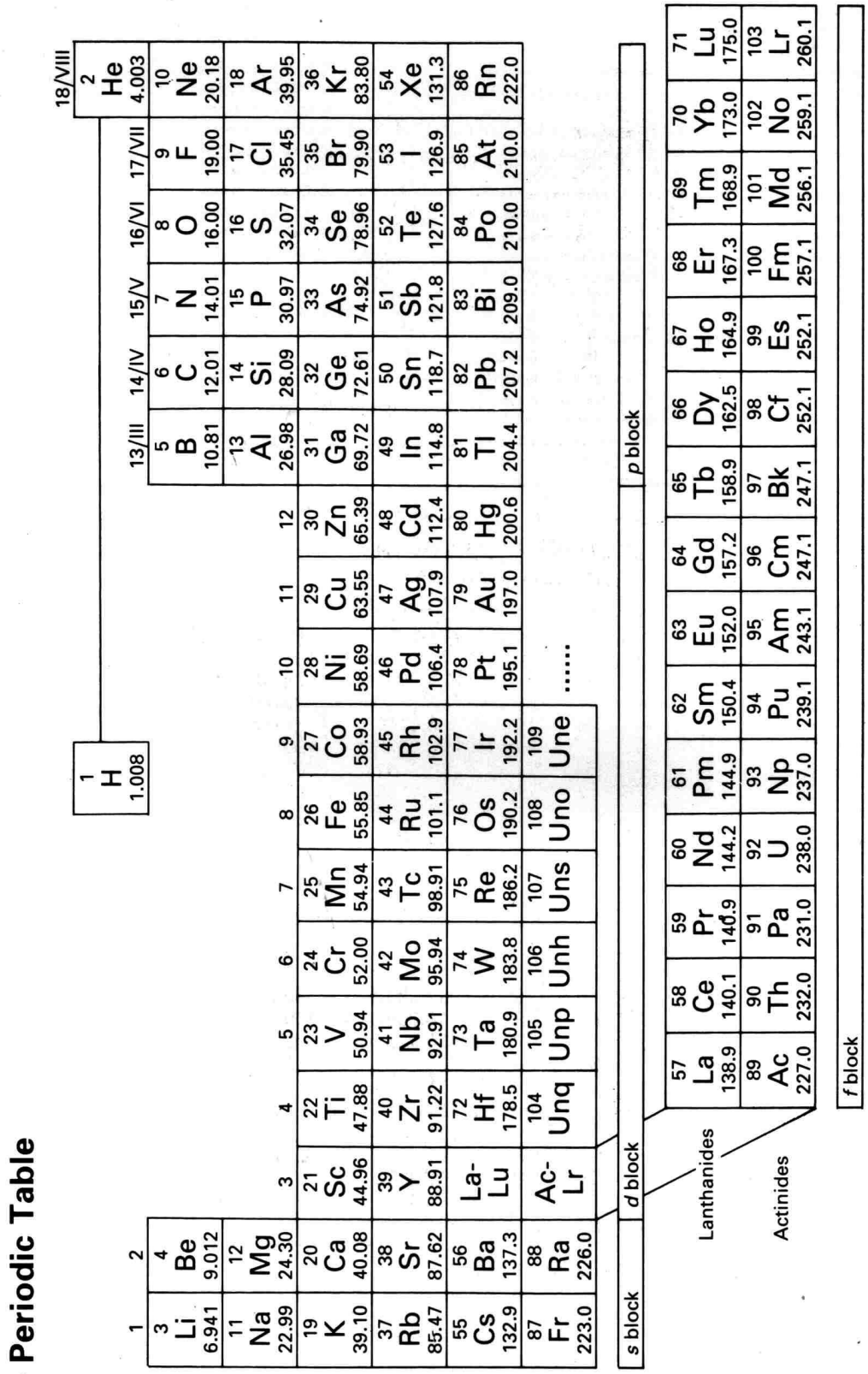
Drago's C_A, E_A, C_B, and E_B values

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 Periodic Table
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1 H 1.008
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
14 Si 28.09
15 P 30.97
16 S 32.07
17 Cl 35.45
18 Ar 39.95
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20 Ca 40.08
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22 Ti 47.88
23 V 50.94
24 Cr 52.00
25 Mn 54.94
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27 Co 58.93
28 Ni 58.69
29 Cu 63.55
30 Zn 65.39
31 Ga 69.72
32 Ge 72.61
33 As 74.92
34 Se 78.96
35 Br 79.90
36 Kr 83.80
37 Rb 85.47
38 Sr 87.62
39 Y 88.91
40 Zr 91.22
41 Nb 92.91
42 Mo 95.94
43 Tc 98.91
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18/VIII
s block
d block
p block
f block
Lanthanides
Actinides