UNIVERSITY OF THE WEST INDIES
MONA, JAMAICA
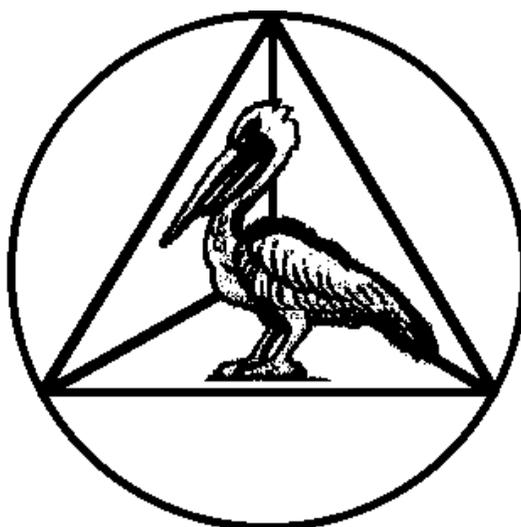
Chemistry of the First Row Transition Metal Complexes
C21J Inorganic Chemistry

http://wwwchem.uwimona.edu.jm/courses/index.html

Prof. R. J. Lancashire
September 2005

Chemistry of the First Row Transition Metal Complexes.

C21J Inorganic Chemistry
24 Lectures 2005/2006

1. Review of Crystal Field Theory. Crystal Field Stabilisation Energies: origin and effects on structures and thermodynamic properties. Introduction to Absorption Spectroscopy and Magnetism. The d^1 case. Ligand Field Theory and evidence for the interaction of ligand orbitals with metal orbitals.

2. Spectroscopic properties of first row transition metal complexes.
a) Electronic states of partly filled quantum levels. l, m_l and s quantum numbers. Selection rules for electronic transitions.
b) Splitting of the free ion energy levels in Octahedral and Tetrahedral complexes. Orgel and Tanabe-Sugano diagrams.
c) Spectra of aquated metal ions. Factors affecting positions, intensities and shapes of absorption bands.

3. Magnetic Susceptibilities of first row transition metal complexes.
a) Effect of orbital contributions arising from ground and excited states.
b) Deviation from the spin-only approximation.
c) Experimental determination of magnetic moments. Interpretation of data.

4. General properties (physical and chemical) of the 3d transition metals as a consequence of their electronic configuration. Periodic trends in stabilities of common oxidation states. Contrast between first-row elements and their heavier congeners.

5. A survey of the chemistry of some of the elements Ti....Cu, which will include the following topics:
a) Occurrence, extraction, biological significance, reactions and uses
b) Redox reactions, effects of pH on the simple aqua ions
c) Simple oxides, halides and other simple binary compounds.
d) Preparation, structures, physical properties, reactions, uses of a variety of simple coordination complexes, eg acacs, acetates, amines, etc.

6. Reaction Mechanisms. Stability and inertness, rates and mechanisms. Classification of inorganic reaction mechanisms. Molecularity in relation to substitution reactions. Square planar substitution; evidence for the 'A' mechanism. The *trans* effect. Octahedral substitution: aquation, anation and base hydrolysis. Electron transfer reactions - inner/outer sphere.

7. Transition metal organometallics. Carbonyls and other π-acceptor ligands; syntheses, structures and bonding and reactions. The EAN rule. Organic ligands: alkyls, alkenes, π-allyls and aromatic ligands including cyclopentadiene. A discussion of synthetic methods, structural and bonding aspects, physical properties, stabilities and important reactions. Catalysis and important industrial uses.

References:
"Complexes and First-Row Transition Elements", Nicholls
"Basic Inorganic Chemistry", Cotton, Wilkinson and Gaus
"Advanced Inorganic Chemistry", Cotton and Wilkinson
"Coordination Compounds", Kettle
"Chemistry of the Elements", Greenwood and Earnshaw
"Concepts and Models of Inorganic Chemistry", Douglas, McDaniel and Alexander

Objectives

The Crystal Filed splitting parameter Δ has been used to correlate a wide range of properties of first-row transition metal complexes. This includes structure, electronic spectra, magnetic properties and some aspects of thermochemistry. It is perhaps the single most useful parameter in understanding coordination chemistry.

This course begins with a review of simple crystal field theory, highlighting both strengths and weaknesses of the model. This model is then extended to the more general ligand field theory and the concept of interelectronic repulsion is introduced followed by a description of Russell-Saunders terms.

Electronic spectra of high-spin octahedral and tetrahedral complexes are interpreted by the use of Orgel diagrams. Spin forbidden bands and low-spin complexes are treated using Tanabe-Sugano diagrams. It is expected that students should be able to interpret all simple electronic spectra and predict both position and intensity based on these diagrams and the appropriate selection rules.

Magnetic properties of high-spin octahedral and tetrahedral complexes are simplified in terms of systems with A and E ground terms or T ground terms. Students are expected to be able to predict variations from the spin-only magnetic moment for these types of coordination complexes. In addition, based on experiments covered in the Laboratory course, they should have a detailed knowledge of the method for experimentally determining a magnetic moment.

The latter part of the course is largely descriptive and covers the occurrence and extraction of the first-row transition metals. This is followed by an in-depth look at the chemistry of a few selected metals in terms of the chemistry of their oxides, and aqua species, halides and simple coordination complexes with ligands such as 2,4 pentanedione and acetate.

An introduction to inorganic reaction mechanisms, a subject that has rapidly grown in importance during the last thirty years, will be presented to you. This introduction is necessarily short (5 lectures) and selective, since the course is primarily concerned with coordination compounds of first row transition metal ions. The primary objective of this part of the course is to make you familiar with the following topics:
    i) current classification of inorganic reaction mechanisms;
    ii) mechanism of substitution at square-planar complexes;
    iii) mechanism of substitution at octahedral complexes;
    iv) mechanism of electron transfer reactions.

A short course (4 lectures) on organometallic chemistry involving only transition metals will also be presented. Again, organometallic chemistry has developed enormously during the last 40 years. Currently approximately half of the world's research publications in chemistry relate to organometallic compounds. Over and above organometallics play a vital role in the economy of the developed nations. The aim of the course is to introduce to you:
(i) the IUPAC nomenclature of organometallic compounds;
(ii) classification based on the 18-electron rule;
(iii) preparations and structures of some metal carbonyls and metallocenes;
(iv) vibrational spectra of metal carbonyls;
(v) Catalysis – hydrogenation and carbonylation.
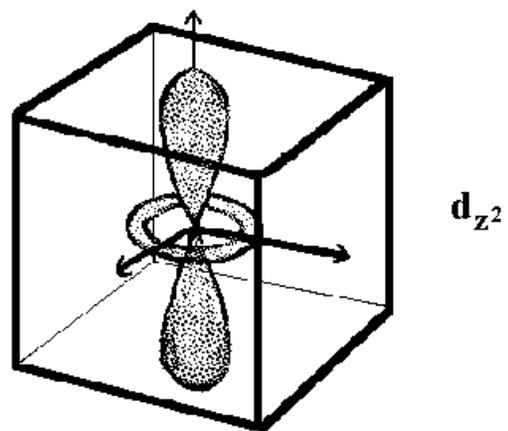
d_{z^2}
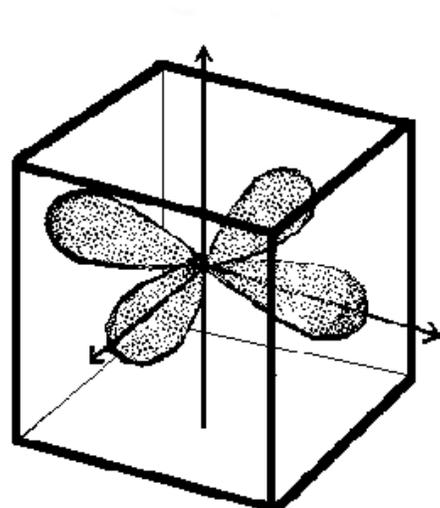
$d_{x^2-y^2}$
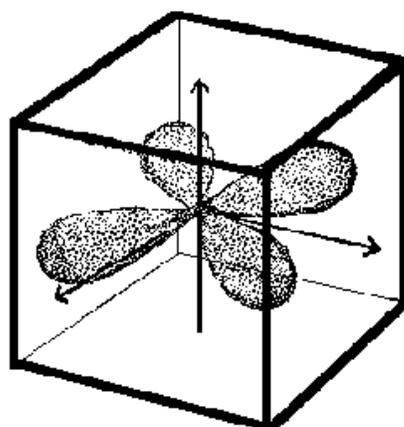
d_{xy}, d_{yz}, d_{xz}
depending on orientation

The orientation of d orbitals towards the faces and edges of a cube.

Crystal field d orbital splitting diagrams for common stereochemistries.

$\Delta_{tet} = 4/9 \; \Delta_{oct}$

$d_{xy} \quad d_{yz} \quad d_{xz}$

Δ_{tet}

$d_{x2-y2} \quad d_{z2}$

Tetrahedral field

free-ion

$d_{x2-y2} \quad d_{z2}$

Δ_{oct}

$d_{xy} \quad d_{yz} \quad d_{xz}$

Octahedral field

d_{x2-y2}

Δ_{oct}

d_{xy}

$d_{yz} \quad d_{xz}$

d_{z2}

Square-planar field

# of d electrons

Energy

- CFSE (Oct)
- CFSE (Tet)
- OSPE
- Zero
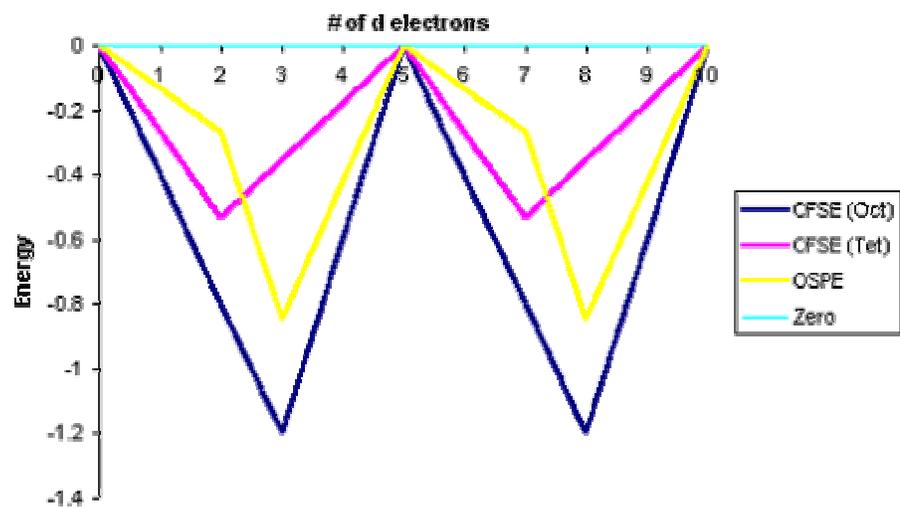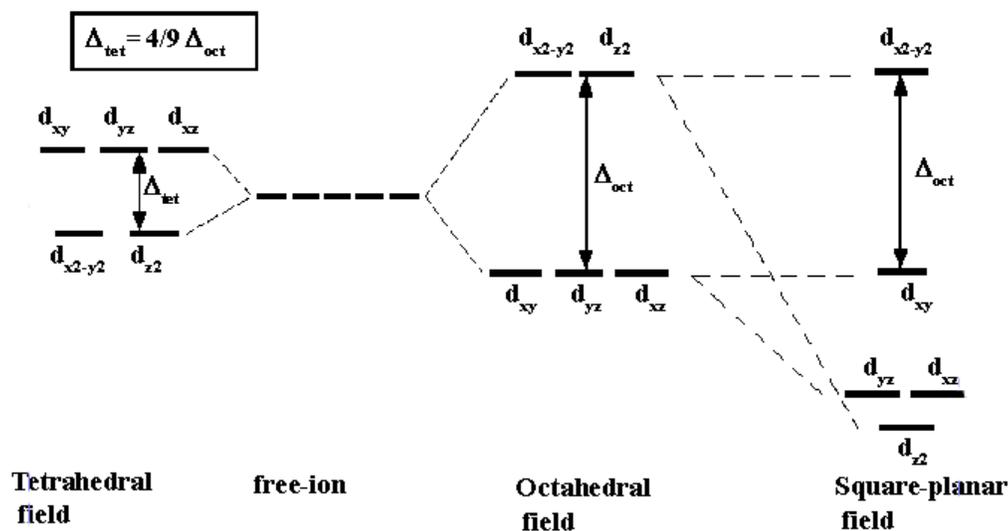
Octahedral Site Preference Energies calculated from Crystal Field Stabilisation Energies for High-Spin Octahedral and Tetrahedral Fields

Crystal Field Stabilization Energies (CFSE)

Config	Octahedral		Tetrahedral		OSPE
	config	CFSE	config	CFSE	
d^1	t_{2g}^1	$-2/5\ \Delta_o$	e^1	$-3/5\ \Delta_t$	$-6/45\ \Delta_o$
d^2	t_{2g}^2	$-4/5\ \Delta_o$	e^2	$-6/5\ \Delta_t$	$-12/45\ \Delta_o$
d^3	t_{2g}^3	$-6/5\ \Delta_o$	$e^2 t_2^1$	$-4/5\ \Delta_t$	$-38/45\ \Delta_o$
d^4	$t_{2g}^3 e_g^1$	$-3/5\ \Delta_o$	$e^2 t_2^2$	$-2/5\ \Delta_t$	$-19/45\ \Delta_o$
d^5	$t_{2g}^3 e_g^2$	$0\ \Delta_o$	$e^2 t_2^3$	$0\ \Delta_t$	$0\ \Delta_o$
d^6	$t_{2g}^4 e_g^2$	$-2/5\ \Delta_o +P$	$e^3 t_2^3$	$-3/5\ \Delta_t +P$	$-6/45\ \Delta_o$
d^7	$t_{2g}^5 e_g^2$	$-4/5\ \Delta_o + P$	$e^4 t_2^3$	$-6/5\ \Delta_t + P$	$-12/45\ \Delta_o$
d^8	$t_{2g}^6 e_g^2$	$-6/5\ \Delta_o +P$	$e^4 t_2^4$	$-4/5\ \Delta_t + P$	$-38/45\ \Delta_o$
d^9	$t_{2g}^6 e_g^3$	$-3/5\ \Delta_o +P$	$e^4 t_2^5$	$-2/5\ \Delta_t + P$	$-19/45\ \Delta_o$
d^{10}	$t_{2g}^6 e_g^4$	$0\ \Delta_o$	$e^2 t_2^3$	$0\ \Delta_t$	$0\ \Delta_o$

Spinels

Spinel is the name given to the mineral $MgAl_2O_4$. It has a common structural arrangement shared by many oxides of the transition metals with formula AB_2O_4. In the **normal** pattern the oxygens form a cubic close packed (face centred) array and the Mg(II) or A(II) and Al(III) or B(III) sit in tetrahedral (1/8 occupied) and octahedral (1/2 occupied) sites in the lattice, giving a Unit Cell with 8 Mg's, 16 Al's and 32 O's.

An **inverse spinel** is an alternative arrangement where half of the trivalent ions swap with the divalent ions so that the M(II) now occupy octahedral sites i.e. $B(AB)O_4$.

OSPE calculations are often able to accurately predict the type of spinel found since they show whether the M(II) or M(III) has the stronger preference for the Octahedral site.

The Irving-Williams series

The general stability sequence of high spin octahedral metal complexes for the replacement of water by other ligands is:

Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)
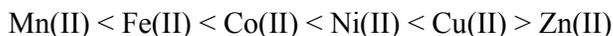
This trend is essentially independent of the ligand.

In the case of 1, 2-diaminoethane (en), the first step-wise stability constants ($logK_1$) for M(II) ions are shown below.

log K versus Z
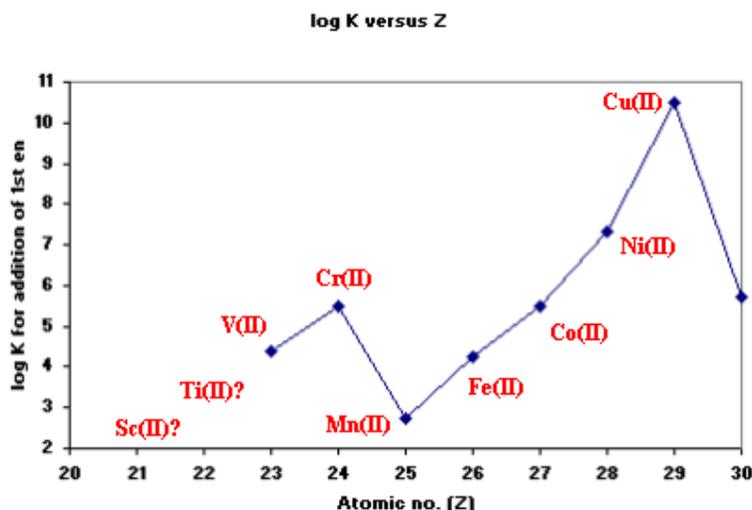
Notes
The sequence is generally quoted ONLY for Mn(II) to Zn(II) since there is little data available for the other first row transition metal ions; their M(II) oxidation states are not very stable.
The position of Cu(II) is considered out-of-line with predictions based on Crystal Field Theory and is probably a consequence of the fact that Cu(II) often forms distorted octahedral complexes. (See notes on the Jahn-Teller effect).

One explanation
Crystal Field Theory is based on the idea that a purely electrostatic interaction exists between the central metal ion and the ligands. This suggests that the stability of the complexes should be related to the ionic potential; that is, the **charge to radius ratio**. In the Irving-Williams series, the trend is based on high-spin M(II) ions, so what needs to be considered is how the ionic radii vary across the d-block.

For free metal ions in the gaseous phase it might be expected that the ionic radius of each ion on progressing across the d-block should show a gradual decrease in size. This would come about due to the incomplete screening of the additional positive charge by the additional electron, as is observed in the **Lanthanide Contraction**. For high-spin octahedral complexes it is essential to consider the effect of the removal of the degeneracy of the d-orbitals by the crystal field. Here the d-electrons will initially add to the lower t_{2g} orbitals before filling the e_g orbitals since for octahedral

complexes, the t_{2g} subset are directed in between the incoming ligands whilst the e_g subset are directed towards the incoming ligands and cause maximum repulsion.

Variation of Ionic Radii
for high-spin octahedral M(II) ions
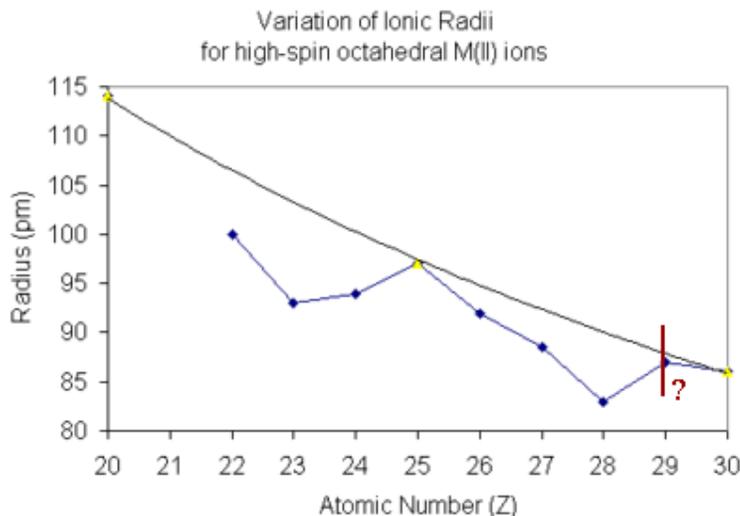
For d^1-d^3 (and d^6-d^8) the addition of the electrons to the t_{2g} orbitals will mean that the screening of the increasing attractive nuclear charge is not very effective and the radius should be smaller than for the free ion.

The position of d^4 and d^9 on the plot is difficult to ascertain with certainty since six-coordinate complexes are expected to be distorted due to the Jahn-Teller Theorem. Cr(II) is not very stable so few measurements are available. For Cu(II) however, many complexes are found to have either 4 short bonds and 2 long bonds or 2 short and 4 long bonds. The radii are expected to show an increase over the d^3 and d^8 situation since electrons are being added to the e_g subset. The reported values have been found to lie on both sides of the predicted value.

For d^0, d^5 and d^{10} the screening expected is essentially that of a spherical arrangement equivalent to the absence of a crystal field. The plot above shows that these points return to the line drawn showing a gradual decrease of the radius on moving across the d-block.

Once the decrease in radius with Z pattern is understood, it is a small step to move to a pattern for q/r since this only involves taking the reciprocal of the radius and holding the charge constant. The radius essentially decreases with increasing Z, therefore 1/r must increase with increasing Z.

For the sequence Mn(II) to Zn(II), the crystal field (q/r) trend expected would be:

Mn(II) < Fe(II) < Co(II) < Ni(II) > Cu(II) > Zn(II)
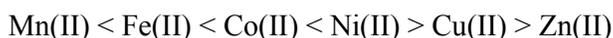
Apart from the position of Cu(II), this corresponds to the Irving-Williams series. The discrepancy is once again accounted for by the fact that copper(II) complexes are often distorted or not octahedral at all. When this is taken into consideration, it is seen that the Irving-Williams series can be explained quite well using Crystal Field Theory.

THE SPECTROCHEMICAL SERIES

One of the important aspects of CFT is that all ligands are not identical when it comes to a causing separation of the d-orbitals. For transition metal compounds, we are well aware of the multitude of colours available for a given metal ion when the ligands or stereochemistry are varied. In octahedral complexes, this can be considered a reflection of the energy difference between the higher d_{z2}, d_{x2-y2} (e_g subset) and the d_{xy}, d_{yz}, d_{xz} (t_{2g} subset).

It has been established that the ability of ligands to cause a large splitting of the energy between the orbitals is essentially independent of the metal ion and the SPECTROCHEMICAL SERIES is a list of ligands ranked in order of their ability to cause large orbital separations.

A shortened list includes:

$$I^- < Br^- < \underline{S}CN^- \sim Cl^- < F^- < OH^- \sim \underline{O}NO^- < C_2O_4^{2-} < H_2O$$
$$< \underline{N}CS^- < EDTA^{4-} < NH_3 \sim pyr \sim en < bipy < phen < CN^- \sim CO$$
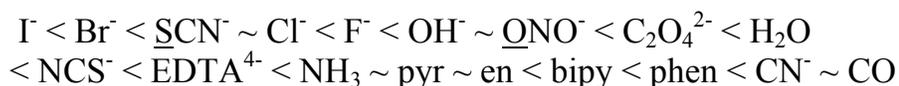
When metal ions that have between 4 and 7 electrons in the d orbitals form octahedral compounds, two possible electron allocations can occur. These are referred to as either weak field - strong field or high spin - low spin configurations.

Breakdown of CFT.

From a purely ionic basis we would expect $CO < H_2O < C_2O_4^{2-} < EDTA^{4-}$

That this is not the case is a reflection of covalent interactions.

metal orbitals σ symmetry	ligand group orbitals	metal orbitals σ symmetry	ligand group orbitals

A_{1g} — s

$\Sigma_a = \frac{1}{\sqrt{6}}(\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z})$

E_g — d_{z^2}

$\Sigma_{z^2} = \frac{1}{2\sqrt{3}}(2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y})$

$d_{x^2-y^2}$

$\Sigma_{x^2-y^2} = \frac{1}{2}(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$

T_{1u}

p_z

$\Sigma_z = \frac{1}{\sqrt{2}}(\sigma_z - \sigma_{-z})$

p_x

$\Sigma_x = \frac{1}{\sqrt{2}}(\sigma_x - \sigma_{-x})$

p_y

$\Sigma_y = \frac{1}{\sqrt{2}}(\sigma_y - \sigma_{-y})$
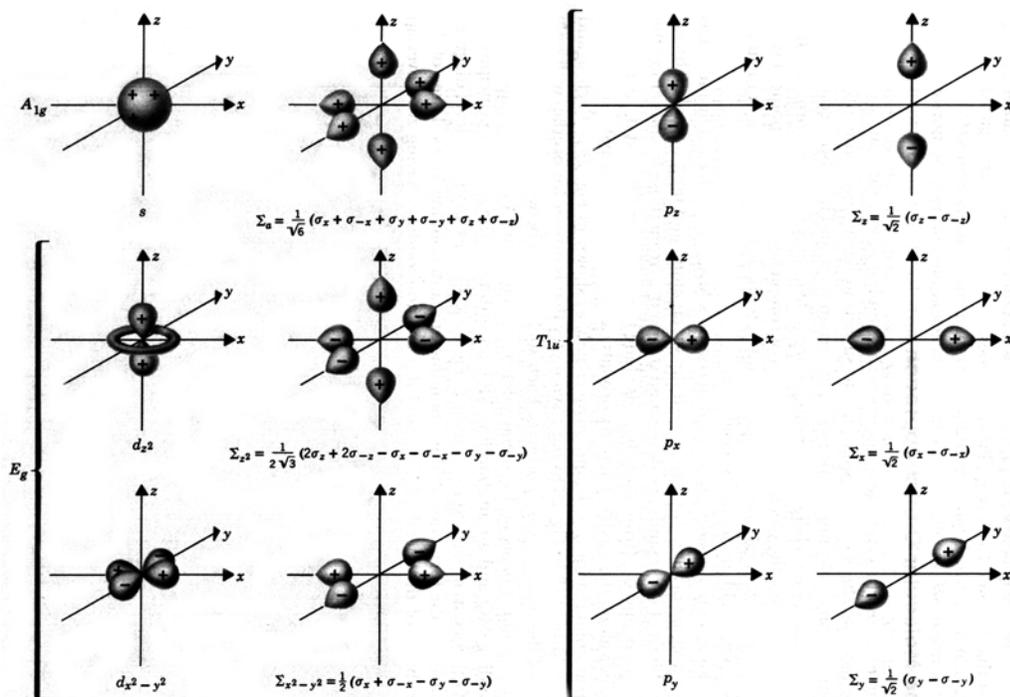
The metal orbitals and ligand group orbitals that can overlap to form σ-molecular orbitals in an ML_6 complex

Molecular-orbital energy-level diagram for a σ-bonded octahedral complex.

Molecular orbitals of complex

Molecular-orbital energy-level diagram for a π-bonded octahedral complex
a) with low-energy filled π-orbitals on the ligand – Δ decreased
b) with high-energy filled π-orbitals on the ligand – Δ increased.

Electronic Spectra of Transition metal complexes.

The Russell Saunders Coupling Scheme

Quantum Numbers
Electrons in an atom reside in shells characterised by a particular value of n, the Principal Quantum Number. Within each shell an electron can occupy an orbital which is further characterised by an Orbital Quantum Number, l, where l can take all values in the range:
$l = 0, 1, 2, 3, ... , (n-1)$,
traditionally termed s, p, d, f, etc. orbitals after the lines in alkali metal spectra:
sharp, principal, diffuse, and fundamental.

Each orbital has a characteristic shape reflecting the motion of the electron in that particular orbital, this motion being characterised by an angular momentum that reflects the angular velocity of the electron moving in its orbital.

A quantum mechanics approach to determining the energy of electrons in an element or ion is based on the results obtained by solving the Schrödinger Wave Equation for the H-atom. The various solutions for the different energy states are characterised by the three quantum numbers, n, l and m_l.

m_l is a subset of l, where the allowable values are: $m_l = l, l-1, l-2, ... 1, 0, -1, ..., -(l-2), -(l-1), -l$.

There are thus $(2l +1)$ values of m_l for each l value,
i.e. one s orbital ($l = 0$), three p orbitals ($l = 1$), five d orbitals ($l = 2$), etc.

There is a fourth quantum number, m_s, that identifies the orientation of the spin of one electron relative to those of other electrons in the system. A single electron in free space has a fundamental property associated with it called spin, arising from the spinning of an asymmetrical charge distribution about its own axis. Like an electron moving in its orbital around a nucleus, the electron spinning about its axis has associated with its motion a well defined angular momentum. The value of m_s is either + ½ or - ½.

In summary then, each electron in an orbital is characterised by four quantum numbers:

Quantum Numbers	
n	Principal Quantum Number - largely governs size of orbital and its energy
l	Azimuthal/Orbital Quantum Number - largely determines shape of orbital
m_l	Magnetic Quantum Number
m_s	Spin Quantum Number - either + ½ or - ½ for single electron

Russell Saunders coupling

The ways in which the angular momenta associated with the orbital and spin motions in many-electron-atoms can be combined together are many and varied. In spite of this seeming complexity, the results are frequently readily determined for simple atom systems and are used to characterise the electronic states of atoms.

The interactions that can occur are of three types.

- spin-spin coupling
- orbit-orbit coupling
- spin-orbit coupling

There are two principal coupling schemes used:

- Russell-Saunders (or L - S) coupling
- and j - j coupling.

In the Russell Saunders scheme it is assumed that
spin-spin coupling > orbit-orbit coupling > spin-orbit coupling.

This is found to give a good approximation for first row transition series where J coupling is ignored, however for elements with atomic number greater than thirty, spin-orbit coupling becomes more significant and the j-j coupling scheme is used.

Spin-Spin coupling
S - the resultant spin quantum number for a system of electrons. The overall spin S arises from adding the individual m_s together and is as a result of coupling of spin quantum numbers for the separate electrons.

Orbit-Orbit coupling
L - the total orbital angular momentum quantum number defines the energy state for a system of electrons. These states or term letters are represented as follows:

Total Orbital Momentum					
L	0	1	2	3	4	5
		S	P	D	F	G	H

Spin-Orbit coupling
Coupling occurs between the resultant spin and orbital momenta of an electron which gives rise to J the total angular momentum quantum number. Multiplicity occurs when several levels are close together and is given by the formula (2S+1).

The Russell Saunders term symbol that results from these considerations is given by:
$$^{(2S+1)}L$$

As an example, for a d^1 configuration:

S= + ½, hence (2S+1) = 2
L=2
and the Russell Saunders Ground Term is written as ^2D

The Russell Saunders term symbols for the other free ion configurations are given in the Table below.

Terms for 3d^n free ion configurations		
Configuration	Ground Term	Excited Terms
d^1, d^9	^2D	-
d^2, d^8	^3F	$^3P, {}^1G, {}^1D, {}^1S$
d^3, d^7	^4F	$^4P, {}^2H, {}^2G, {}^2F, 2 \times {}^2D, {}^2P$
d^4, d^6	^5D	$^3H, {}^3G, 2 \times {}^3F, {}^3D, 2 \times {}^3P, {}^1I, 2 \times {}^1G, {}^1F, 2 \times {}^1D, 2 \times {}^1S$
d^5	^6S	$^4G, {}^4F, {}^4D, {}^4P, {}^2I, {}^2H, 2 \times {}^2G, 2 \times {}^2F, 3 \times {}^2D, {}^2P, {}^2S$

Note that d^n gives the same terms as d^{10-n}

Hund's Rules
The Ground Terms are deduced by using Hund's Rules.
The two rules are:
1) The Ground Term will have the maximum multiplicity
2) If there is more than 1 Term with maximum multipicity, then the Ground Term will have the largest value of L.

A simple graphical method for determining just the ground term alone for the free-ions uses a "fill in the boxes" arrangement.

d^n	2	1	0	-1	-2	L	S	Ground Term
d^1	↑					2	1/2	^2D
d^2	↑	↑				3	1	^3F
d^3	↑	↑	↑			3	3/2	^4F
d^4	↑	↑	↑	↑		2	2	^5D
d^5	↑	↑	↑	↑	↑	0	5/2	^6S
d^6	↑↓	↑	↑	↑	↑	2	2	^5D
d^7	↑↓	↑↓	↑	↑	↑	3	3/2	^4F
d^8	↑↓	↑↓	↑↓	↑	↑	3	1	^3F
d^9	↑↓	↑↓	↑↓	↑↓	↑	2	1/2	^2D

To calculate **S**, simply sum the **unpaired** electrons using a value of ½ for each.
To calculate **L**, use the labels for each column to determine the value of **L** for that box, then add all the individual box values together.
For a d^7 configuration, then:
in the +2 box are 2 electrons, so **L** for that box is 2*2= 4
in the +1 box are 2 electrons, so **L** for that box is 1*2= 2
in the 0 box is 1 electron, **L** is 0
in the -1 box is 1 electron, **L** is -1*1= -1
in the -2 box is 1 electron, **L** is -2*1= -2

Total value of **L** is therefore +4 +2 +0 -1 -2 or **L**=3.

Note that for 5 electrons with 1 electron in each box then the total value of **L** is 0.
This is why **L** for a d^1 configuration is the same as for a d^6.

The other thing to note is the idea of the "hole" approach.
A d^1 configuration can be treated as similar to a d^9 configuration. In the first case there is 1 electron and in the latter there is an absence of an electron ie a hole.

The overall result shown in the Table above is that:
4 configurations (d1, d4, d6, d9) give rise to D ground terms,
4 configurations (d2, d3, d7, d8) give rise to F ground terms
and the d5 configuration gives an S ground term.

The Crystal Field Splitting of Russell-Saunders terms

The effect of a crystal field on the different orbitals (s, p, d, etc.) will result in splitting into subsets of different energies, depending on whether they are in an octahedral or tetrahedral environment. The magnitude of the d orbital splitting is generally represented as a fraction of Δ_{oct} or 10Dq.

The ground term energies for free ions are also affected by the influence of a crystal field and an analogy is made between orbitals and ground terms that are related due to the angular parts of their electron distribution. The effect of a crystal field on different orbitals in an octahedral field environment will cause the d orbitals to split to give t_{2g} and e_g subsets and the D ground term states into T_{2g} and E_g, (where upper case is used to denote states and lower case orbitals). f orbitals are split to give subsets known as t_{1g}, t_{2g} and a_{2g}. By analogy, the F ground term when split by a crystal field will give states known as T_{1g}, T_{2g}, and A_{2g}.

Note that it is important to recognise that the F ground term here refers to states arising from d orbitals and not f orbitals and depending on whether it is in an octahedral or tetrahedral environment the lowest term can be either A_{2g} or T_{1g}.

The Crystal Field Splitting of Russell-Saunders terms in high spin octahedral crystal fields.	
Russell-Saunders Terms	**Crystal Field Components**
S	A_{1g}
P	T_{1g}
D	E_g , T_{2g}
F	A_{2g} , T_{1g} , T_{2g}
G	A_{1g} , E_g , T_{1g} , T_{2g}
H	E_g , 2 x T_{1g} , T_{2g}
I	A_{1g} , A_{2g} , E_g , T_{1g} , T_{2g}

Note that, for simplicity, spin multiplicities are not included in the table since they remain the same for each term.

The table above shows that the Mulliken symmetry labels, developed for atomic and molecular orbitals, have been applied to these states but for this purpose they are written in CAPITAL LETTERS.

Mulliken Symbols	
Mulliken Symbol for atomic and molecular orbitals	**Explanation**
a	Non-degenerate orbital; symmetric to principal C_n
b	Non-degenerate orbital; unsymmetric to principal C_n
e	Doubly degenerate orbital
t	Triply degenerate orbital
(subscript) g	Symmetric with respect to center of inversion
(subscript) u	Unsymmetric with respect to center of inversion
(subscript) 1	Symmetric with respect to C_2 perp. to principal C_n
(subscript) 2	Unsymmetric with respect to C_2 perp. to principal C_n
(superscript) '	Symmetric with respect to s_h
(superscript) "	Unsymmetric with respect to s_h

 For splitting in a tetrahedral crystal field the components are similar, except that the symmetry label g (gerade) is absent.

The ground term for first-row transition metal ions is either D, F or S, which in high spin octahedral fields gives rise to A, E or T states. This means that the states are either non-degenerate, doubly degenerate or triply degenerate.

Representations of the three types of f orbitals
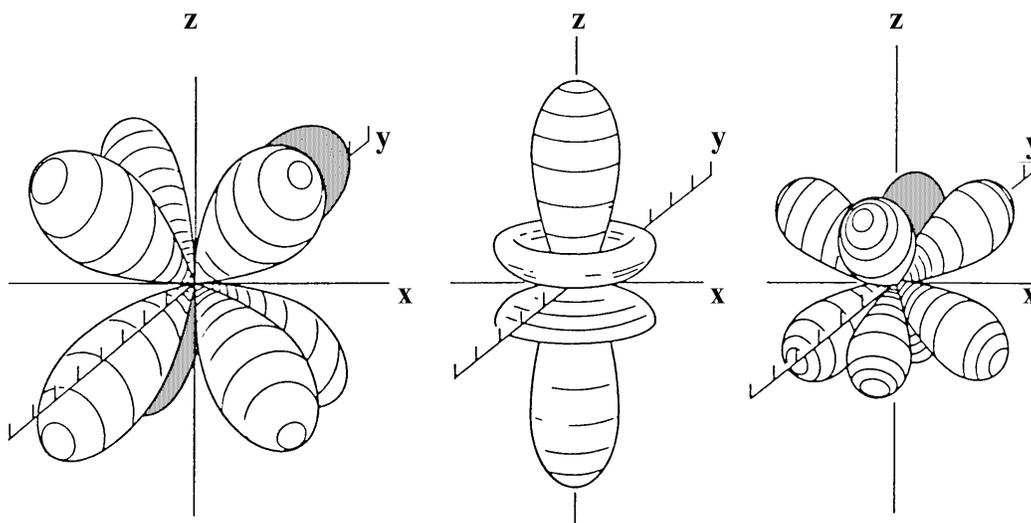
Effect of an Octahedral Crystal Field on the three types of f orbitals

$f_{z(5z2-3r2)}$, $f_{y(5y2-3r2)}$, $f_{x(5x2-3r2)}$
$f_{z(x2-y2)}$, $f_{y(z2-x2)}$, $f_{x(y2-z2)}$
f_{xyz}

$f_{z(5z2-3r2)}$
$f_{y(5y2-3r2)}$
$f_{x(5x2-3r2)}$

$+3/5\Delta$

$4/5\Delta$

$9/5\Delta$

$-1/5\Delta$

$f_{z(x2-y2)}$
$f_{y(z2-x2)}$
$f_{x(y2-z2)}$

Δ

$-6/5\Delta$

f_{xyz}

7 f orbitals in the free-ion

in an octahedral crystal field
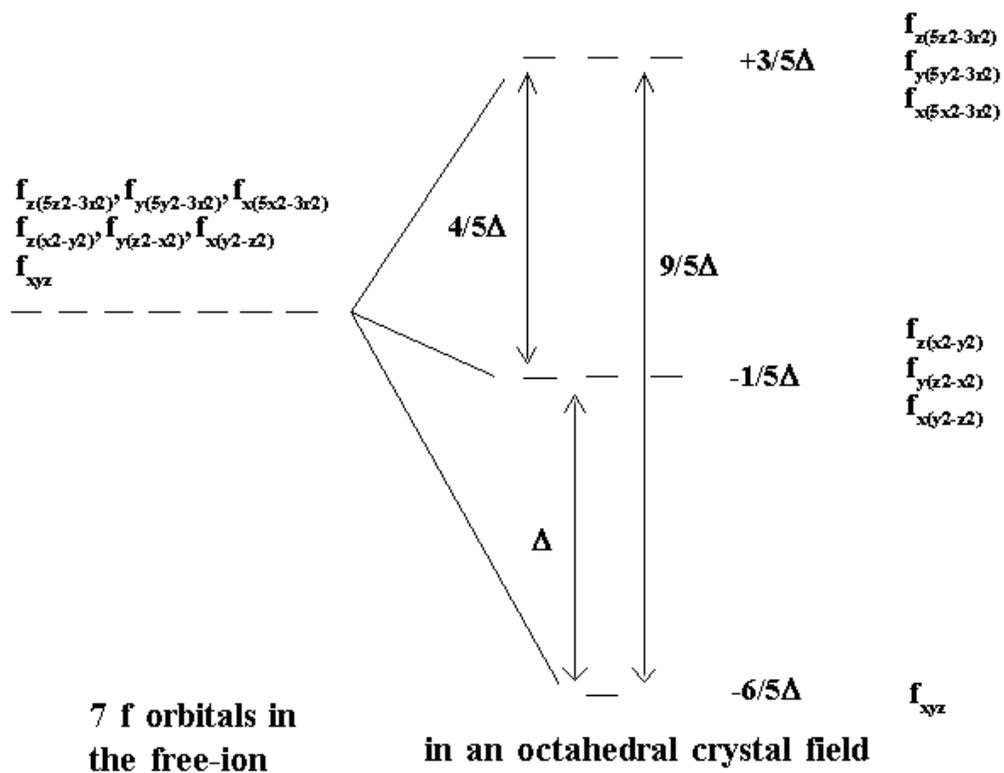
Selection Rules

For allowed transitions:
$\Delta S = 0$ The Spin Rule
$\Delta l = +/- 1$ The Orbital Rule (Laporte)

The first rule says that allowed transitions involve the promotion of electrons without a change in their spin.

The second rule says that transitions within a given set of p or d orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are forbidden if the molecule has a centre of symmetry.

Relaxation of the Rules can occur through:

a) Spin-Orbit coupling - this gives rise to weak spin forbidden bands
b) Vibronic coupling - an octahedral complex may have allowed vibrations where the molecule is asymmetric. Absorption of light at that moment is then possible.
c) π-acceptor and π-donor ligands can mix with the d-orbitals so transitions are no longer purely d-d.

Types of transition
1) Charge transfer, either ligand to metal or metal to ligand often extremely intense and found in the UV but may have a tail into the visible.
2) d-d can occur in both UV and visible, weak transitions.

Intensities

	Example	Typical value of ε m^2 mol^{-1}
Spin forbidden, Laporte forbidden	$Mn(H_2O)_6{}^{2+}$	0.1
Spin allowed, Laporte forbidden	$Ti(H_2O)_6{}^{3+}$	1
Spin allowed, Laporte partially allowed by d-p mixing	$CoCl_4{}^{2-}$	50
Spin allowed, Laporte allowed	$TiCl_6{}^{2-}$	1000
e.g. charge transfer bands	$MnO_4{}^{-}$	

Orgel diagrams for First-Row Transition Metal Ions

d^1,d^6 tetrahedral   d^1,d^6 octahedral

d^4,d^9 octahedral   d^4,d^9 tetrahedral
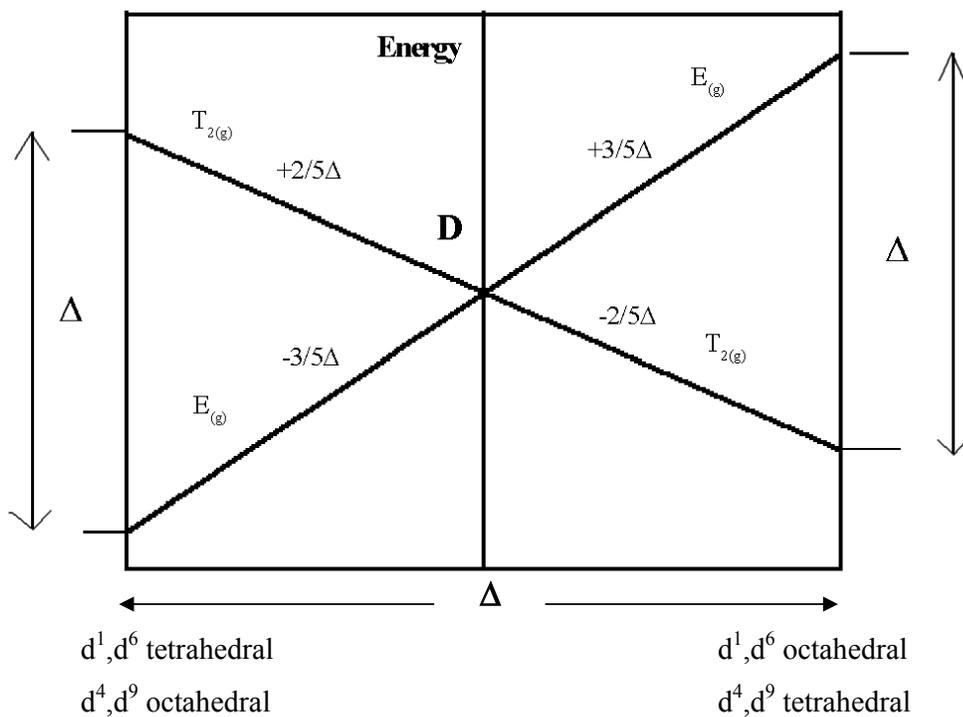
The splitting of free-ion D terms in octahedral and tetrahedral fields.

d^2,d^7 tetrahedral   d^2,d^7 octahedral

d^3,d^8 octahedral   d^3,d^8 tetrahedral
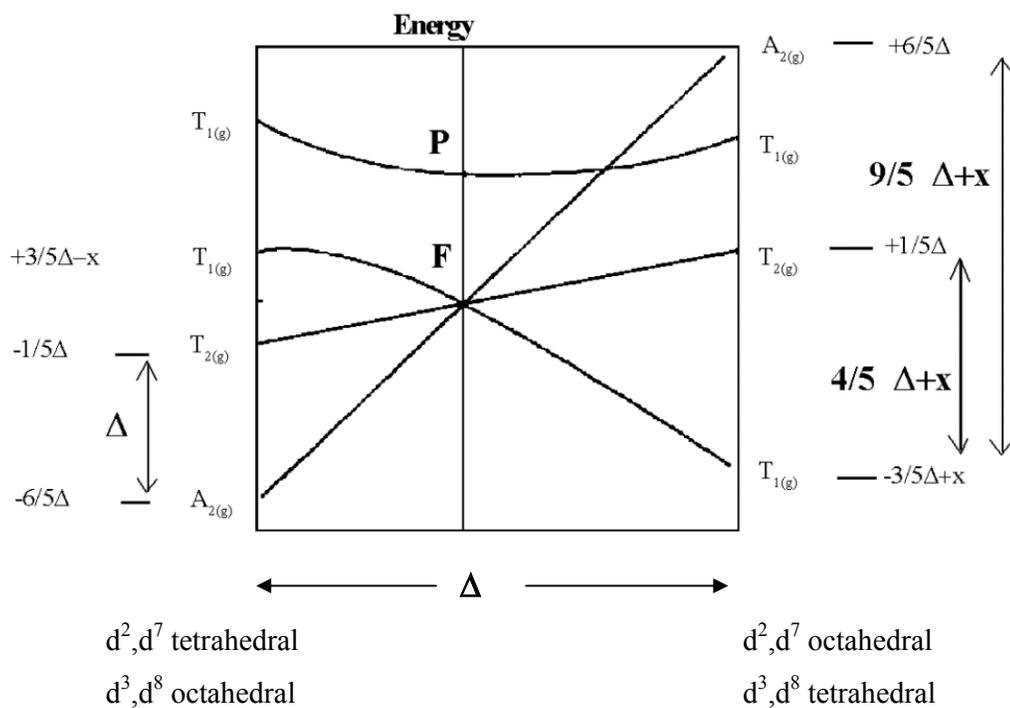
The splitting of free-ion F and P terms in octahedral and tetrahedral fields.

Electronic spectra of some Cr³⁺ solutions

ε
$m^2\ mol^{-1}$

$[Cr(en)_3]^{3+}$

$[Cr(H_2O)_6]^{3+}$

$[Cr(CN)_6]^{3-}$

35,000   30,000   25,000   20,000   15,000   10,000

$\upsilon\ (cm^{-1})$

25,000   12,500   10,000   8,000

ε
$m^2\ mol^{-1}$

1.4

1.2

1.0

0.8

0.6

0.4

0.2

$[Ni(DMF)_6]^{2+}$

$[Ni(DMA)_6]^{2+}$

$[Ni(NH_3)_6]^{2+}$

400   600   800   1000   1200   1400

Wavelength (nm)
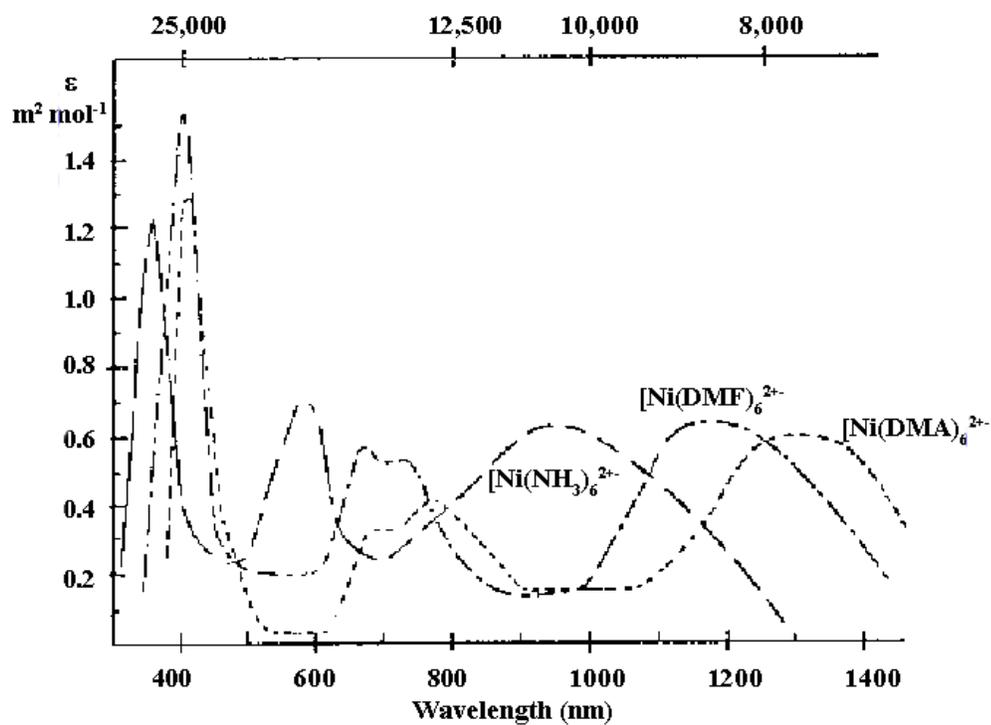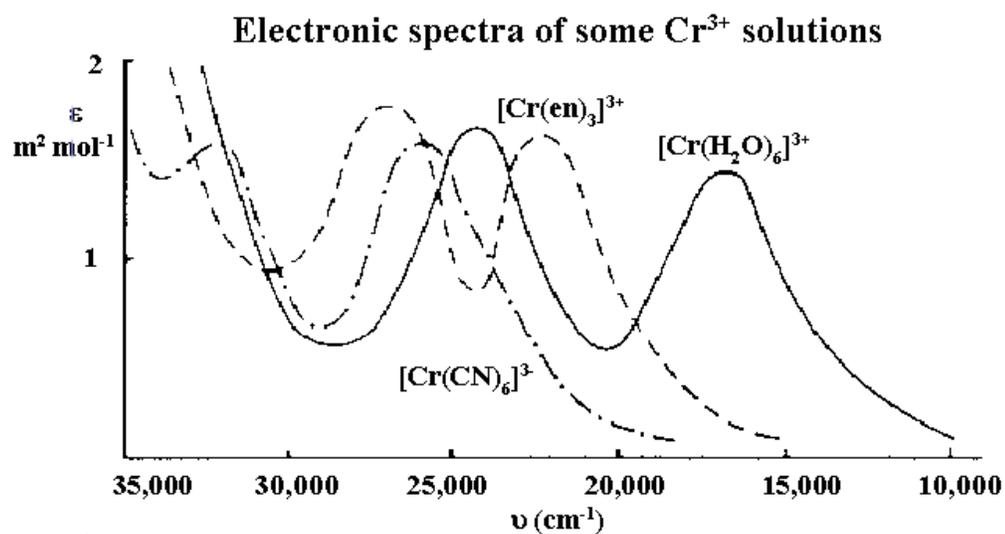
Electronic spectra of some Ni²⁺ solutions

Complex Ion   **Free Ion**
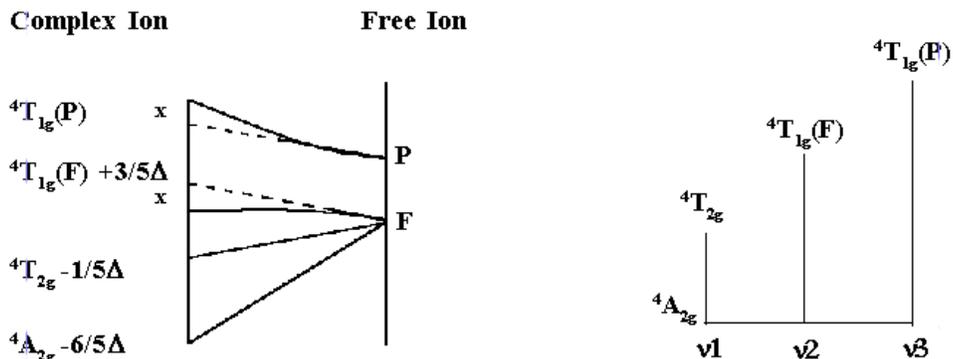
For d^3, d^8 octahedral and d^2, d^7 tetrahedral complexes, the above diagrams can be used to interpret the observed electronic absorption spectra. Take for example the Cr^{3+} aquo ion $[Cr(H_2O)_6]^{3+}$. The spectrum consists of 3 bands found at 17,000 cm^{-1}, 24,000 cm^{-1} and 37,000 cm^{-1}.

$\nu1$ corresponds to Δ and since the lowest band is found at 17,000 cm^{-1} then this gives us Δ directly from the spectrum.

The next band is found at 24,000 cm^{-1} and this can be equated to:
$\nu2 = 9/5\Delta - x$ where x is the configuration interaction between the T(F) state and the T(P) state of the same symmetry. Since Δ is 17,000 and $\nu2$ is observed at 24,000 then x must be 6,600 cm^{-1}.

The last band is seen at 37,000 cm^{-1} and here
$\nu3 = 6/5\Delta + 15B + x$ where B is one of the RACAH parameters. Solving for B gives a value of $B = 667$ cm^{-1}. For the free Cr3+ ion B is 1030 cm^{-1} so that in the complex this term is reduced by ~2/3 of the free ion value.
A large reduction in B indicates a strong Nephelauxetic Effect. The Nephelauxetic Series is:

$$F- > H_2O > urea > NH_3 > en \sim C_2O_4^{2-} > NCS- > Cl- \sim CN- > Br- > S^{2-} \sim I-$$
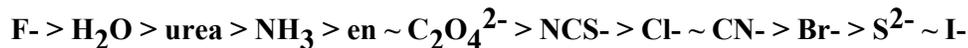
Ionic ligands such as F- give a small reduction in B, while covalently bonded ligands such as I- give a large reduction of B.

Free Ion   **Complex Ion**

$^4A_{2g} + 6/5\Delta$

$^4T_{1g}(P)$

$^4T_{2g} + 1/5\Delta$

$^4T_{1g} - 3/5\Delta - x$

$^4A_{2g}$

$^4T_{1g}(P)$

$^4T_{2g}$

$^4T_{1g}$

$\nu1$ $\nu2$ $\nu3$

$^4T_{1g}(P)$

$^4A_{2g}$

$^4T_{2g}$

$^4T_{1g}$

$\nu1$ $\nu2$ $\nu3$
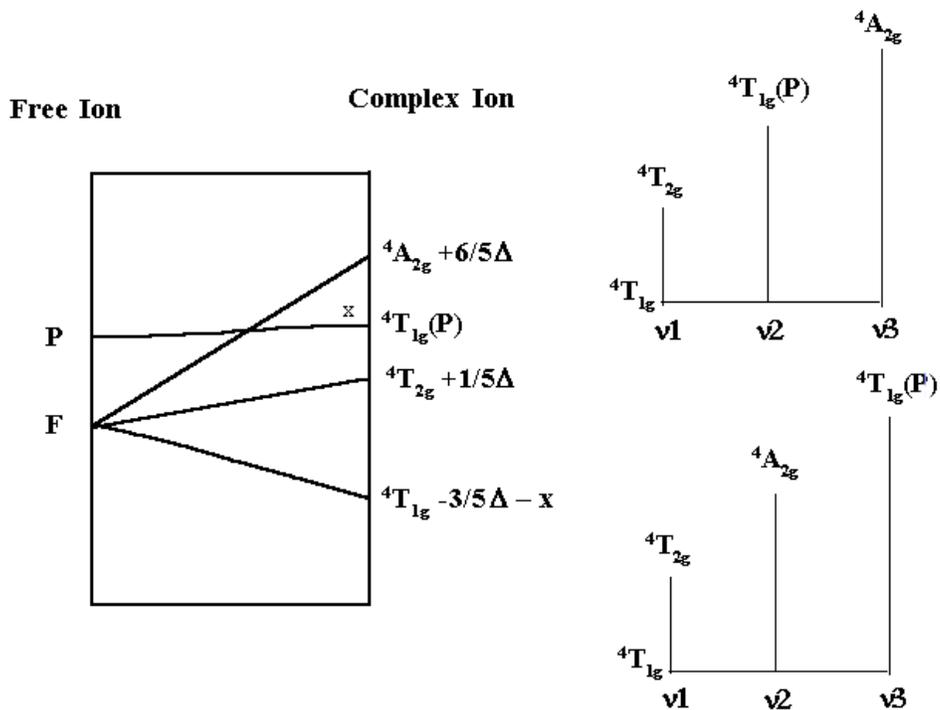
For d^2, d^7 octahedral and d^3, d^8 tetrahedral complexes, the above diagrams can be used to interpret the observed electronic absorption spectra. Note that the transitions that occur are dependent on the sizes of Δ and B and the A_{2g} term may be either higher or lower than the T_{1g} (P) term.

Take for example, $KCoF_3$ which contains the Co in a high spin $[CoF_6]$ environment. The spectrum consists of 3 bands found at 7,150 cm^{-1}, 15,200 cm^{-1} and 19,200 cm^{-1}.

$\nu1$ corresponds to $4/5\Delta + x$ and in both cases would correspond to a transition between the $^4T_{1g}$ and $^4T_{2g}$. The second band at 15,200 cm^{-1} is assigned to the transition to $^4A_{2g}$ that is, the diagram used is the lower one on the right above and corresponds to $9/5\Delta + x$. The difference between these two bands gives a Δ value of 8050 cm^{-1}. x can therefore be calculated as 710 cm^{-1}. Convince yourself that this assignment is better than the alternative.

$\nu3 = 15B' + 3/5\Delta + 2x = 19,200$ and since Δ is 8050 and x is 710 cm^{-1} then solving for B gives a value of B=863cm^{-1} . In the free ion B is 970 cm^{-1} so that in the complex this term is reduced by 89% of the free ion value.

$^4T_{1g}(P)$ $^4A_{2g}$ $^4T_{2g}$ $^4T_{1g}$ ν1 ν2 ν3

$Co(H_2O)_6^{2+}$

$^4T_1(P)$ $^4T_1(F)$ $^4T_2$ $^4A_2$ ν1 ν2 ν3

$CoCl_4^{2-}$
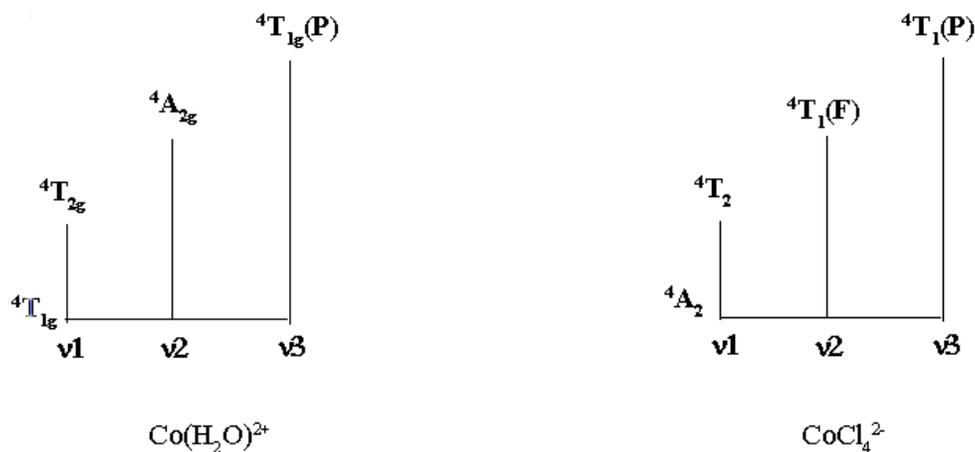
The colour of Co(II) complexes has interested chemists for many years and the pale-pink, octahedral to bright-blue, tetrahedral colour change is seen in such devices as weather guides and in the dye in silica gel in the laboratory.

Assignment of the bands for these spectra can present some problems however.

For the aqua ion, a band is observed at around 8000 cm^{-1} and a broad band centred around 20,000 cm-1 (ε for these bands are less than 1 m^2 mol^{-1}).

The lowest energy band must correspond to:

$$^4T_{2g} \longleftarrow {}^4T_{1g}$$

which leaves the bands at 16,000, 19,400 and 21,600 cm^{-1} to be assigned.

A tentative assignment puts the

$$^4T_{1g}(P) \longleftarrow {}^4T_{1g}$$

transition at 19,400 and hence the 16,000 band is due to

$$^4A_{2g} \longleftarrow {}^4T_{1g}$$
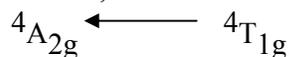
The band at 21,600 cm^{-1} is believed to come from spin-orbit effects.

From this Δ ~ 9000 cm^{-1} and B ~ 900 cm^{-1}.

In the tetrahedral case, using Δt =4/9 Δo then we predict that the transition

$$^4T_2 \longleftarrow {}^4A_2$$

should be observed below 4000 cm^{-1}. Only 2 bands are seen and they occur at 5,800 and 15,000 cm^{-1}. (ε value for the 15,000 band is ~60 m^2 mol^{-1}). The first must therefore correspond to

$$^4T_1(F) \longleftarrow {}^4A_2$$

and the second to

$$^4T_1(P) \longleftarrow {}^4A_2$$

23
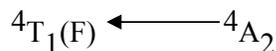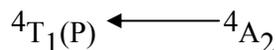
Electronic spectra of $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$

$\varepsilon\ m^2\ mol^{-1}$

$[Co(H_2O)_6]^{2}$

0.6

0.4

0.2

$[CoCl_4]^{2-}$

60

40

20

25,000   20,000 15,000 10,000   5000

wavelength (cm^{-1})
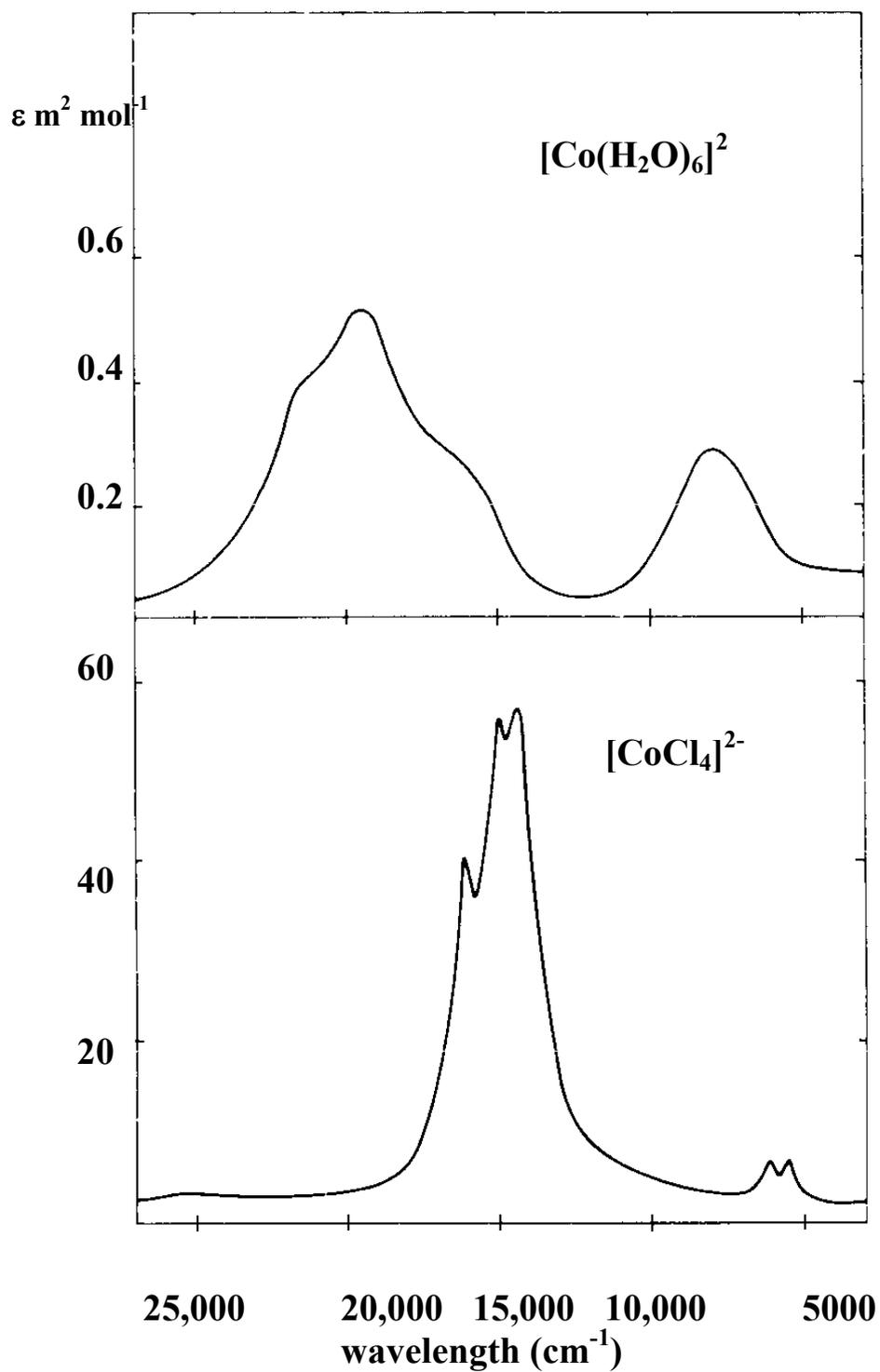
Tanabe-Sugano Diagrams

The use of Orgel diagrams allows a qualitative description of the spin-allowed electronic transitions expected for states derived from D and F ground terms. Only 2 diagrams are needed for high spin d2-d9 and both tetrahedral and octahedral ions are covered.

Tanabe-Sugano diagrams were developed in the 1950's to give a semi-quantitative approach and include both high and low spin ions and not only the spin-allowed transitions but the spin-forbidden transitions as well.

At first glance they can appear quite daunting, but in practice they are much easier to use for interpreting spectra and provide much more information. The obvious differences are the presence of the additional lines and that the ground state is shown as the base line along the X axis rather than as a straight line or curve originating from the Y axis.

On the X axis Δ/B' is plotted while on the Y axis E/B' is plotted, where B' is the modified Racah B parameter that exists in the complex.

A separate diagram is needed for each electronic configuration d2-d9 and for the d4-d7 cases both the high spin and low spin electronic configurations are shown. The high spin is on the left-hand-side of the vertical line on the diagram.

For the d2 case where it is difficult to use an Orgel diagram, the TS diagram is shown below. The ground state is $^3T_{1g}$ which is plotted along the base line.
Note that the transitions that occur are dependent on the sizes of Δ and B and the A_{2g} term may be either higher or lower than the T_{1g} (P) term (depending on whether Δ/B' is greater than about 15).

For the V(III) aqua ion, transitions are observed at 17,200 and 25,600 cm^{-1} which are assigned to the $^3T_{2g}$ <- $^3T_{1g}$ and $^3T_{1g}(P)$ <- $^3T_{1g}$ (F) respectively.
Interpretation requires taking the ratio of these frequencies and then finding the position on the diagram where the height of the $^3T_{1g}(P) / {}^3T_{2g}$ exactly matches that ratio.

For a ratio of 1.49, this is found on the diagram below at Δ/B' of 28.5.

Reading off the position on the Y axis for the three spin-allowed lines gives E/B' values of 25.9, 38.6 and 52 ($^3T_{2g}$, $^3T_{1g}$ and $^3A_{2g}$)

To determine the value of Δ and B' is now relatively straightforward since from the first transition energy of 17,200 cm^{-1} and the value of E/B' of 25.9 we can equate B' as:
B' = 17,200/ 25.9 or B' = 665 cm^{-1}

The value of Δ can then be determined from the Δ/B' ratio of 28.0 and the value just calculated for B' of 665 cm^{-1}.
This gives Δ as 28.0 x 665 = 18,600 cm^{-1}

The transition $^3A_{2g} <- {}^3T_{1g}$ would be predicted to occur at 52 x 665 that is 34,580 cm^{-1} which is in the UV region and not observed. (Possibly obscured by charge transfer bands).

The values of Δ and B' can be compared to similar V(III) complexes and it should be noted that in general for M(III) ions the Δ value is often about 3/2 times the value expected for M(II) ions.

The free ion value of B for a V(III) ion is 860 cm^{-1} and the reduction of this value noted for the observed B' is a measure of what is described as the Nephelauxetic Effect.

d2 Tanabe-Sugano diagram
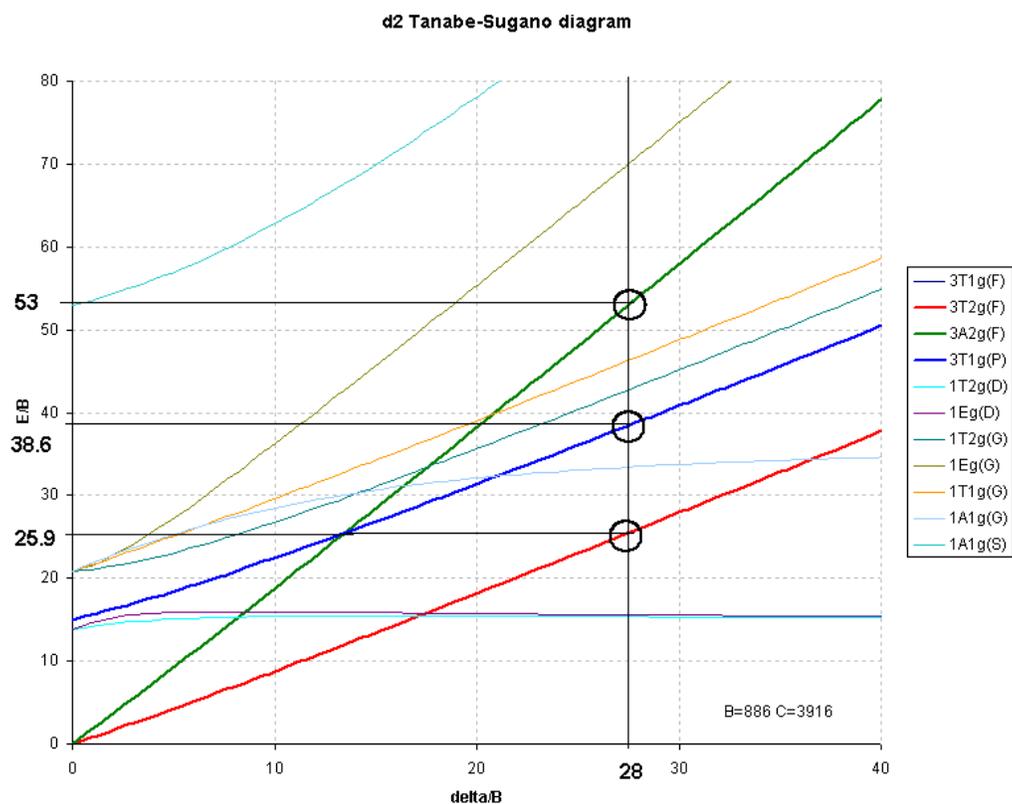
Tanabe-Sugano diagram for the octahedral d^2 case

Based on the known values of ν_1 and ν_2 and the position where the experimental ratio of ν_2/ν_1 is found on the diagram the E/B values are read off the Y-axis.
Then B can be calculated and from the x-axis value then Δ can be determined.

Magnetism

The classical theory of magnetism was well developed before quantum mechanics. Lenz's Law states that: when a substance is placed within a magnetic field, H, the field within the substance, B, differs from H by the induced field, which is proportional to the intensity of magnetisation.

$$B = H + 4\pi I$$

where B is the magnetic field within the substance
H is the applied magnetic field
and I is the intensity of magnetisation

It is usually more convenient to measure mass (gram) susceptibility, Xg, which is related to the volume susceptibility through the density.

$$Xg = \kappa/\rho$$

where ρ is the density.

Finally to get our measured quantity on a basis that can be related to atomic properties, we convert to a molar susceptibility

$$Xm = Xg * RMM$$

Since this value includes the underlying diamagnetism of paired electrons, it is necessary to add the diamagnetic portion of Xm to get a corrected paramagnetic susceptibility.

$$\chi_m \text{ (corrected)} = \chi_m + \chi_{dia}$$

Examples of these corrections are tabulated in the Laboratory Manual.

Normal paramagnetic substances obey Curies Law

$$X = C/T$$

where C is the Curie constant. Thus a plot of 1/X versus T should give a straight line of slope 1/C passing through the origin (0K).

Many substances give a straight line that intercepts just a little above 0K and these are said to obey the Curie-Weiss Law:

$$X = C/(T+\phi)$$

where ϕ is known as the Weiss constant.

The constant C is given by the Langevin expression which relates the susceptibility to the magnetic moment:

$$Xm = N\mu^2 / 3kT$$

where N is Avogadro's number
k is the Boltzmann constant
and T the absolute temperature

rewriting this gives the magnetic moment as

$$\mu = 2.828 \, (\chi_m \, T)^{1/2}$$

From a quantum mechanics viewpoint, the magnetic moment is dependent on both spin and orbital angular momentum contributions. The spin-only formula used last year was given as:

$$\mu_{s.o.} = (4S(S+1))^{1/2}$$

and this can be modified to include the orbital angular momentum

$$\mu_{S+L} = (4S(S+1) + L(L+1))^{1/2}$$

An orbital angular momentum contribution is expected when the ground term is triply degenerate i.e. a T state. These show temperature dependence as well

For A and E states no direct orbital angular momentum is expected but small variations to the magnetic moment are predicted from the equation:

$$\mu_{eff} = \mu \, s.o. \, (1 - \alpha\lambda/\Delta)$$

where α is a constant 2 for E and 4 for A

λ is the spin-orbit coupling constant which although generally not available does give important information since the sign of the value varies depending on the orbital occupancy.
for d^1 to d^4 the value is positive hence μ eff is less than μ s.o.
for d^6 to d^9 the value is negative hence μ eff is greater than μ s.o.

Δ is the crystal field splitting factor which again is often not available for complexes.

Analytical Balance

Draft Shield

Thermometer

Sample

S   N

Magnet

The GOUY technique

Microanalytical balance

Vacuum container

Sample

S   N
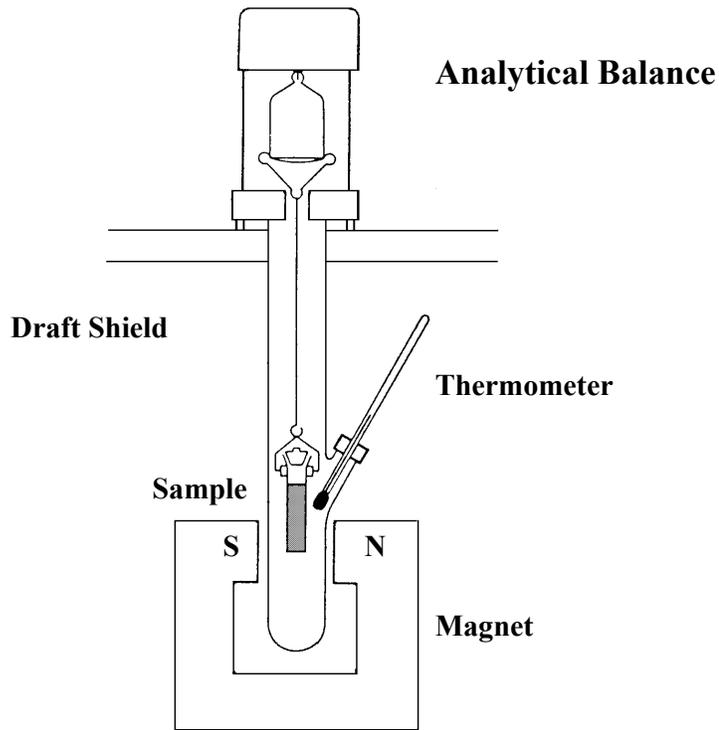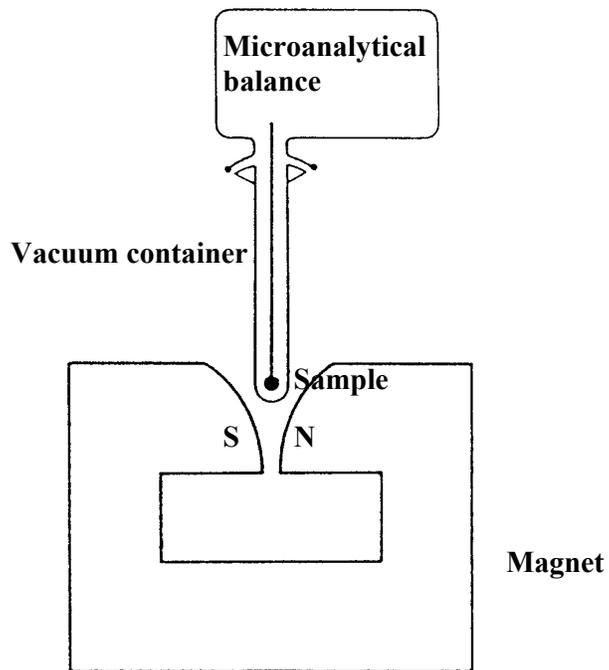
Magnet

The FARADAY Method
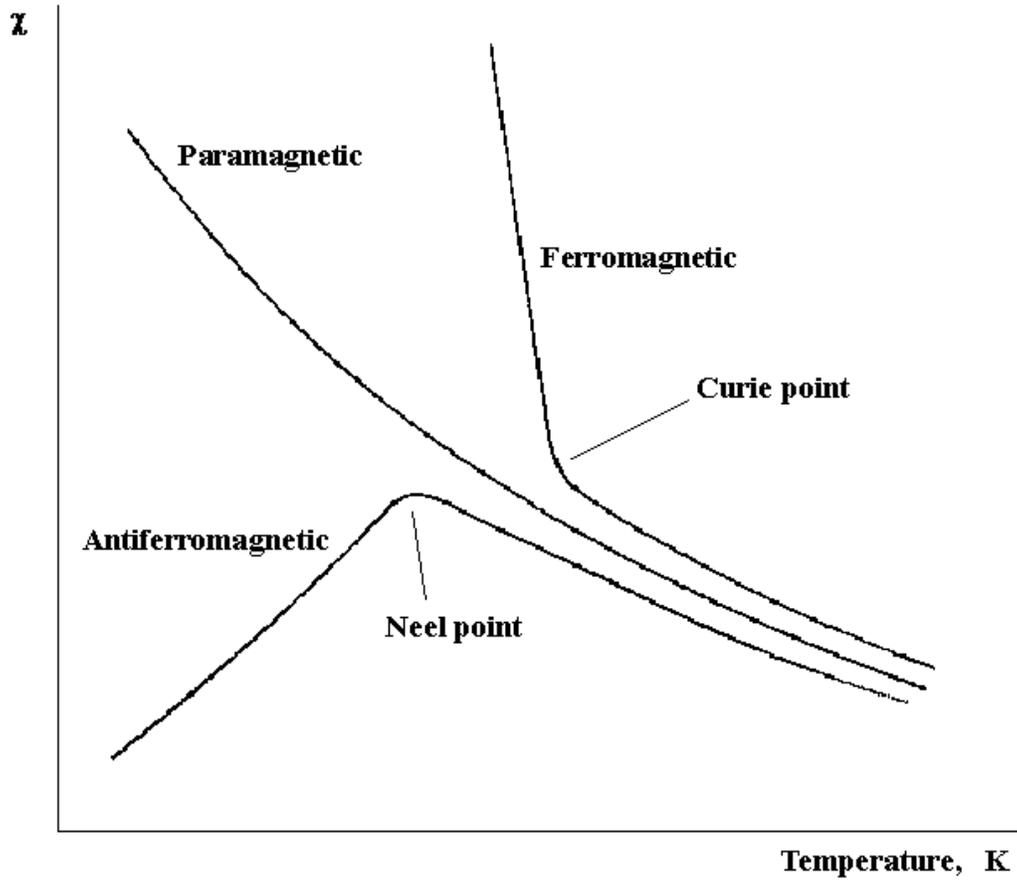
Normal paramagnetic substances obey the Curie Law

$\chi = C/T$

and a plot of 1/c against T gives a straight line of slope 1/C passing through the origin (0K), others obey the Curie-Weiss Law and intercept the Temperature axis a little above or below 0K.

$\chi = C/(T+\theta)$

where C is known as the Curie constant and θ is the Weiss constant.

Comparison of calculated spin-only and spin+orbital magnetic moments with experimental data for some selected octahedral complexes

Ion	Config	OAM ?	μ_{so}	μ_{obs}	μ_{S+L}
Ti(III)	d^1	yes	1.73	1.6-1.7	3.00
V(IV)	d^1	yes	1.73	1.7-1.8	
V(III)	d^2	yes	2.83	2.7-2.9	4.47
Cr(IV)	d^2	yes	2.83	2.8	
V(II)	d^3	no	3.88	3.8-3.9	5.20
Cr(III)	d^3	no	3.88	3.7-3.9	
Mn(IV)	d^3	no	3.88	3.8-4.0	
Cr(II)	d^4 h.s	no	4.90	4.7-4.9	5.48
Cr(II)	d^4 l.s.	yes	2.83	3.2-3.3	
Mn(III)	d^4 h.s	no	4.90	4.9-5.0	
Mn(III)	d^4 l.s.	yes	2.83	3.2	
Mn(II)	d^5 h.s	no	5.92	5.6-6.1	5.92
Mn(II)	d^5 l.s	yes	1.73	1.8-2.1	
Fe(III)	d^5 h.s	no	5.92	5.7-6.0	
Fe(III)	d^5 l.s	yes	1.73	2.0-2.5	
Fe(II)	d^6 h.s	yes	4.90	5.1-5.7	5.48
Co(II)	d^7 h.s	yes	3.88	4.3-5.2	5.20
Co(II)	d^7 l.s	no	1.73	1.8	
Ni(III)	d^7 l.s	no	1.73	1.8-2.0	
Ni(II)	d^8	no	2.83	2.9-3.3	4.47
Cu(II)	d^9	no	1.73	1.7-2.2	3.00

Comparison of calculated spin-only and spin+orbital magnetic moments with experimental data for some selected tetrahedral complexes

Ion	Config	OAM ?	μ_{so}	μ_{obs}	μ_{S+L}
Cr(V)	d^1	no	1.73	1.7-1.8	
Mn(VI)	d^1	no	1.73	1.7-1.8	
Cr(IV)	d^2	no	2.83	2.8	
Mn(V)	d^2	no	2.83	2.6-2.8	
Fe(V)	d^3 h.s	yes	3.88	3.6-3.7	5.20
Mn(II)	d^5 h.s	no	5.92	5.9-6.2	
Fe(II)	d^6 h.s	no	4.90	5.3-5.5	
Co(II)	d^7	no	3.88	4.2-4.8	
Ni(II)	d^8	yes	2.83	3.7-4.0	5.47

h.s = high spin (weak field); l.s = low spin (strong field)
NB: there are no low spin tetrahedral complexes
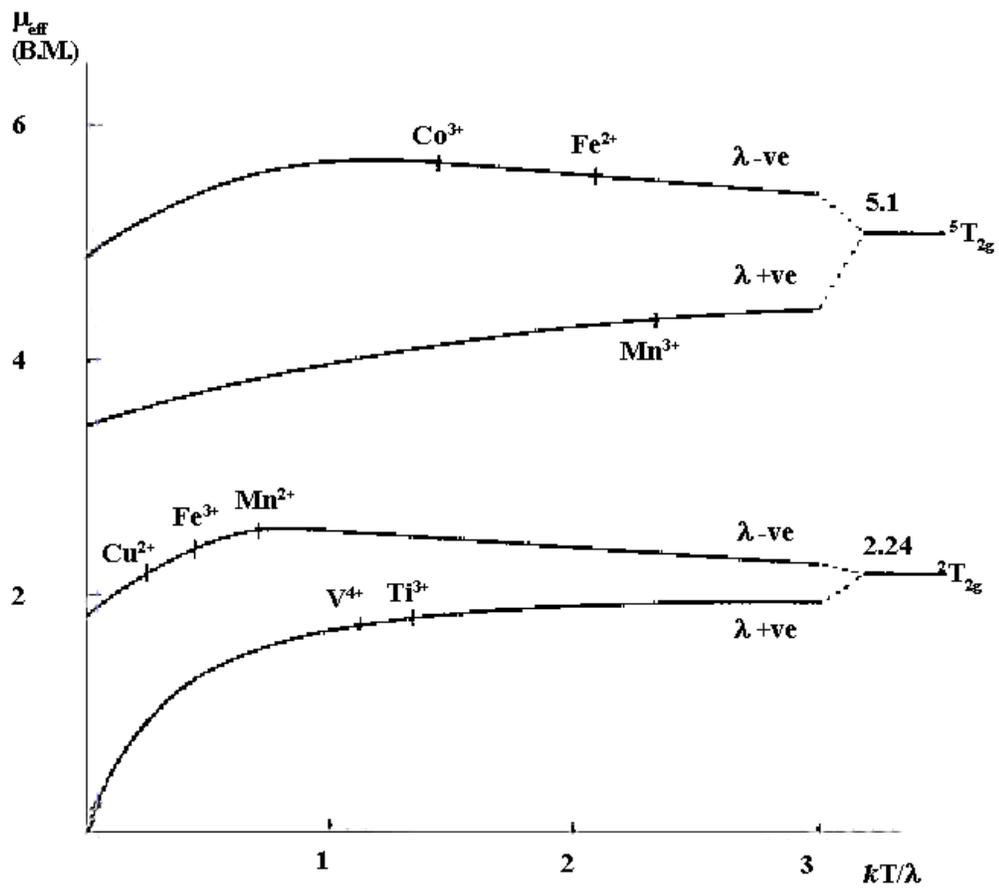
Kotani Plot
The variation of magnetic moment with temperature for d electron T terms.

First Row Transition Metal Halides, Oxides and representative complexes.

Halides

All the 3d elements form dihalides with all halogens, with the exceptions of TiF_2 and CuI_2 . The instability of TiF_2 is probably due to easy disproportionation to Ti and TiF_3 whereas the oxidising power of Cu^{2+} (reducing power of I-) explains the lack of the copper salt. Anhydrous dihalides can generally be synthesised by reaction of metal with hydrogen halide or by dehydration of hydrated salts with a covalent halogen compound. Thermal dehydration normally gives some hydrolysis and a product contaminated with oxides, but pyrolytic dehydration in a stream of hydrogen halide usually gives the anhydrous dihalide.

The difluorides commonly have rutile structures, the dichlorides $CdCl_2$ structures and the diiodides CdI_2 structures. Dibromides have either $CdCl_2$ or CdI_2 structures or both. Dihalides are all ionic and typically dissolve in water to give aquo complexes or mixed aquo-halo-complexes. The solutions of Ti(II), V(II) and Cr(II) are very strongly reducing. They react extremely rapidly with O_2, and Ti(II) even rapidly reduces water to liberate hydrogen. Solutions of Fe(II) undergo slow oxidation in air, but in acid or neutral solution Mn(II), Co(II), Ni(II), and Cu(II) are quite stable to oxygen.

All trihalides of all elements from Ti to Cr are known. Mn(III) and Co(III) are too oxidising to coexist with any halide except F- under ambient conditions, whereas Ti(III) and V(III) are moderately strongly reducing. Chromium(III) is fairly stable toward either reduction or oxidation. There is a marked tendency toward decreasing ionic character on passing from left to right across the period and from the fluorides to the heavier halides. Ferric chloride and bromide show essentially covalent behaviour such as low MPs and solubility in donor organic solvents.

Many trihalides can be prepared by direct combination of the elements. In those cases where direct combination gives a higher oxidation state, trihalides can be produced by either thermal dissociation, disproportionation of the higher halide or by reduction- for example $TiCl_3$ can be prepared by reduction of $TiCl_4$ with H_2 at high temps.

All these trihalides adopt structures in which the metal is six-coordinate, either octahedral or distorted octahedral. Many of the lattices are complicated, but can be represented as $CrCl_3$ or BiI_3 types.

Tetrahalides are formed by Ti and V. The Ti tetrahalides are fairly unreactive in redox and halogenation chemistry, unlike the V compounds. VCl_4 and VBr_4 dissociate spontaneously under ambient conditions to VX_3 and X_2. They also tend to halogenate organic material.

The only stable pentahalide is VF_5 which is readily hydrolysed and a strong Lewis acid. In the solid state it is probably tetrameric with bridging fluorides but in the vapour phase it has a trigonal-bipyramid monomeric structure.

Oxides

All of the 3d elements from Ti to Cu form a monoxide, either by direct combination of the elements or by reduction of a higher oxide by the metal. Most of these have the NaCl structure and are basic. With the exception of TiO, they all dissolve in mineral

acids to give stable salts or complexes of M(II) ions. The Ti^{2+} ion liberates hydrogen from aqueous acid and so dissolution of TiO gives Ti^{3+} and hydrogen.

The monoxides show a variety of physical properties. Thus Ti and V are quasi-metallic, CrO is marginal but Mn to Cu are typical ionic insulators (or more precisely, semiconductors).

All the elements from Ti to Fe give stable M_2O_3 oxides with corundum-type structures. These oxides are all ionic and predominantly basic. In air the M_2O_3 is the most stable oxide for Cr, Mn and Fe.

The elements Ti,V,Cr and Mn give MO_2 oxides with rutile or distorted rutile structures. Note that CrO2 is ferromagnetic and used for the production of magnetic tapes.

The higher oxidation state oxides are good oxidising agents with $V_2O_5 < CrO_3 < Mn_2O_7$ getting progressively more acidic also.

Mixed oxidation state species $M(II)M(III)_2O_4$ are formed by a number of elements, many of which adopt the spinel structure. The spinel structure, named after a mineral form of $MgAl_2O_4$ and of generic formula AB_2O_4 may be approximated as a cubic close packed lattice of oxide ions with one-eighth of the tetrahedral holes occupied by the A(II) ions and one-half of the octahedral holes occupied by the B(III) ions. Closely related and of great interest as far as a fundamental understanding of structure is concerned, is the Inverse Spinel structure. Here there is a site change between the A(II) ions and half of the B(III) ions. Given the fact that this occurs, it is evident that the energy factors directing the two different ions to the different sites are not overwhelmingly large, and it is not surprising that such structures are highly susceptible to defects in actual crystals. One important factor that can influence this site selectivity is the crystal field stabilisation energy of transition metal ions.

Extraction of Iron in a Blast Furnace

The significant reactions occurring within the Blast Furnace can be described via the following steps:

The Blast Furnace	
At 500 C $3Fe_2O_3 + CO -> 2Fe_3O_4 + CO_2$ $Fe_2O_3 + CO -> 2FeO + CO_2$ At 850 C $Fe_3O_4 + CO -> 3FeO + CO_2$ At 1000 C $FeO + CO -> Fe + CO_2$ At 1300 C $CO2 + C -> 2CO$ At 1900 C $C + O_2 -> CO_2$ $FeO + C -> Fe + CO$	

Halides

Titanium

	Colour	MP	BP	μ (BM)	Structure
TiF_4	white	-	284		fluoride bridged
$TiCl_4$	colourless	-24	136.5		-
$TiBr_4$	yellow	38	233.5		-monomeric cf. SnI_4
TiI_4	violet-black	155	377		-

They can all be prepared by direct reaction of Ti with halogen gas (X_2). All are readily hydrolysed.

TiF_3	blue	950d		1.75	
$TiCl_3$	violet	450d		-	BiI_3
$TiBr_3$	violet			-	BiI_3
TiI_3	violet-black			-	

These are prepared by reduction of TiX_4 with H_2.

Vanadium

	Colour	MP	BP	μ(BM)	Structure
VF_5	white	19.5	48.3	0	

Prepared by reaction of V with F_2 in N_2 or with BrF_3 at 300C

VF_4	lime-green	100 [a]	-	1.68	-
VCl_4	red-brown	-25.7	148	1.61	tetrahedral
VBr_4	purple	-23d	-	-	-

[a] sublimes with decomposition at 100 C

VCl_4 is prepared by reaction of V with chlorinating agents such as Cl_2, $SOCl_2$, $COCl_2$ etc.
Reaction of VCl_4 with HF in CCl_3F at -78C gives VF_4

Chromium

	Colour	MP	M-X (pm)	μBM[b]	Structure
CrF_3	green	1404	190		
$CrCl_3$	red-violet	1152	238		$CrCl_3$
$CrBr_3$	green-black	1130	257		BiI_3
CrI_3	black	>500d	-		

[b] all 3.7-4.1 BM

CrX_3 are prepared from Cr with X_2, dehydration of $CrCl_3.6H_2O$ requires $SOCl_2$ at 650C.

CrF_2	green	894		4.3	distorted rutile
$CrCl_2$	white	820-824		5.13	distorted rutile
$CrBr_2$	white	844			
CrI2	red-brown	868			

Reduction of CrX_3 with H_2/HX gives CrX_2.

Manganese

	Colour	MP	BP	μ(BM)	Structure
MnF_2	pale-pink	920	-	-	rutile
$MnCl_2$	pink	652	1190	5.73	$CdCl_2$
$MnBr_2$	rose	695	-	5.82	
MnI_2	pink	613	-	5.88	CdI_2

Prepared from $MnCO_3 + HX \rightarrow MnX_2 + CO_2 + H_2O$

Iron

	Colour	MP	BP	μ(BM)	Structure
FeF_3	green	1000 sublimes			
$FeCl_3$	black	306 sublimes			BiI_3
$FeBr_3$	dark-red-brown	-			BiI_3

Prepared by reaction of $Fe + X_2 \rightarrow FeX_3$.
Note that $FeBr_3$.aq when boiled gives $FeBr_2$

	Colour	MP	BP	μ(BM)	Structure
FeF_2	white	1000	1100	-	rutile
$FeCl_2$	pale yellow-grey	670-674		5.87	$CdCl_2$
$FeBr_2$	yellow-green	684		5.71	CdI_2
FeI_2	grey	red heat		5.75	CdI_2

Fe +HX at red heat -> FeX_2 for X=F,Cl and Br
$Fe + I_2 \rightarrow FeI_2$

Cobalt

	Colour	MP		μ(BM)	Structure
CoF_2	pink	1200		-	rutile
$CoCl_2$	blue	724		5.47	$CdCl_2$
$CoBr_2$	green	678			CdI_2
CoI_2	blue-black	515			CdI_2

Co or $CoCO_3 + HX \rightarrow CoX_2$.aq $\rightarrow CoX_2$

Nickel

	Colour	MP		μ(BM)	Structure
NiF_2	yellow	1450		2.85	tetragonal rutile
$NiCl_2$	yellow	1001		3.32	$CdCl_2$
$NiBr_2$	yellow	965		3.0	$CdCl_2$
NiI_2	Black	780		3.25	$CdCl_2$

$Ni + F_2$ 55C/slow -> NiF_2; $Ni + Cl_2$ EtOH/20 C -> $NiCl_2$
$Ni + Br_2$ red heat -> $NiBr_2$; $NiCl_2 + 2NaI$ -> $NiI_2 + 2 NaCl$

Copper

	Colour	MP	BP	μ (BM)	Structure
CuF_2	white	950d	-	1.5	
$CuCl_2$	brown	632	993d	1.75	$CdCl_2$
$CuBr_2$	black	498	-	1.3	

Copper(II) halides are moderate oxidising agents due to the Cu(I)/ Cu(II) couple. In water, where the potential is largely that of the aquo-complexes, there is not a great deal of difference between them, but in non-aqueous media, the oxidising (halogenating) power increases in the sequence $CuF_2 << CuCl_2 << CuBr_2$.

$Cu + F_2$ -> CuF_2; $Cu + Cl_2$/ 450 C -> $CuCl_2$; $Cu + Br_2$ -> $CuBr_2$
or from CuX_2.aq by heating -> CuX_2

CuCl	white	430	1359	
CuBr	white	483	1345	
CuI	white	588	1293	Zinc Blende

Reduction of CuX_2 -> CuX except for F which has not been obtained pure.
Note that $Cu(II)I_2$ can not be isolated due reduction to CuI.

Oxides and Aquo Species

Titanium

		MP	
TiO_2	rutile	1892	Refractive Index 2.61-2.90 cf. Diamond 2.42

obtained from hydrolysis of TiX_4 or Ti(III) salts. TiO_2 reacts with acids and bases. $TiOSO_4$ formed in H_2SO_4 (Titanyl sulfate)

In Base:
$MTiO_3$ metatitanates (eg Perovskite, $CaTiO_3$ and ilmenite, $FeTiO_3$)
$M2TiO_4$ orthotitanates

Peroxides are highly coloured and can be used for colourimetric analysis.
pH <1 $[TiO_2(OH)(H_2O)x]+$
pH 1-2 $[(O_2)Ti-O-Ti(O_2)](OH)_x^{2-x}$, x=1-6

$$Ti(H_2O)_6^{3+} \rightarrow \quad Ti(OH)(H_2O)_5^{2+} \quad + \quad H+ \quad\quad pK=1.4$$

$$TiO^{2+} + 2H+ + \quad e- \quad \rightarrow \quad Ti^{3+} \quad + \quad H_2O \quad\quad E=0.1V$$
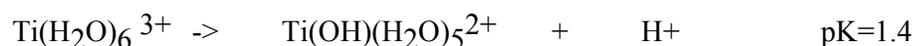
Vanadium

	Colour	Common Name	Oxid. State	MP	V-O distance (pm)
V_2O_5	brick-red	pentoxide	V^{5+}	658	158.5-202
V_2O_4	blue	dioxide	V^{4+}	1637	176-205
V_2O_3	grey-black	sesquioxide	V^{3+}	1967	196-206

V_2O_5 is the final product of the oxidation of V metal, lower oxides etc.

Aqueous Chemistry very complex:
In alkaline solution,

VO_4^{3-}	+	H+	->	HVO_4^{2-}		
$2HVO_4^{2-}$			->	$V_2O_7^{4-}$	+	H_2O
HVO_4^{2-}	+	H+	->	H_2VO_4-		
$3H_2VO_4^-$			->	$V_3O_9^{3-}$	+	$3H_2O$
$4H_2VO_4^-$			->	$V_3O_{12}^{4-}$	+	$4H_2O$

In acidic solution,

$10V_3O_9^{3-}$	+	15H+	->	$3HV_{10}O_{28}^{5-}$	+	$6H_2O$
H_2VO_4-	+	H+	->	H_2VO_4		
$HV_{10}O_{28}^{5-}$	+	H+	->	$H_2V_{10}O_{28}^{4-}$		
H_3VO_4	+	H+	->	VO_2^+	+	$2H_2O$
$H_2V_{10}O_{28}^{4-}$	+	14H+	->	$10VO_2^+$	+	$8H_2O$

$VO(H_2O)_4SO_4$
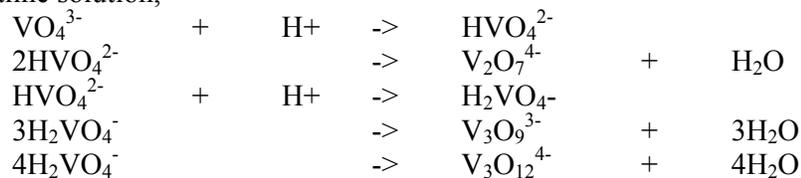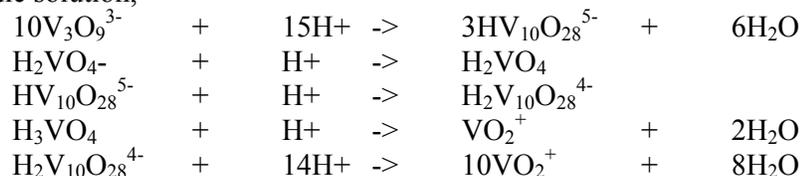
The crystal structure of this salt was first determined in 1965. The V=O bond length was 159.4pm, the aquo group trans to this had the longest V-O bond length (228.4pm) and the equatorial bond lengths were in the range 200.5-205.6 pm. Note that SO42- was coordinated in an equatorial position.

The IR stretching frequency for the V=O in vanadyl complexes generally occurs at 985 +/- 50 cm-1.

Redox properties of oxovanadium ions:

VO_2^+ + 2H+ +e- -> VO^{2+} + H2O E=1.0v

VO^{2+} + 2H+ +e- -> V^{3+} + H2O E=0.34V
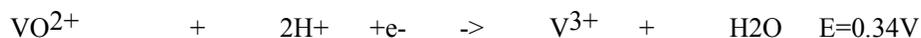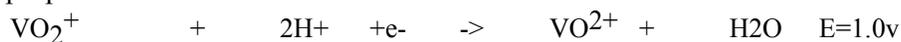
Chromium

	Colour	Oxidation State	MP	
CrO_3	deep red	Cr^{6+}	197d	
Cr_3O_8				
Cr_2O_5		intermediate		
Cr_5O_{12}		etc		
CrO_2	brown-black	Cr^{4+}	300d	
Cr_2O_3	green	Cr^{3+}	2437	-antiferromagnetic < 35 C

Dichromate and chromate equilibria is pH dependent:

$HCrO_4^-$ - > CrO_4^{2-} + H+ $K=10^{-5.9}$

H_2CrO_4 -> $HCrO_4^-$ + H+ $K=10^{+0.26}$

$Cr_2O_7^{2-}$ + H2O -> $2HCrO_4^-$ $K=10^{-3.2}$

$HCr_2O_7^-$ -> $Cr_2O_7^{2-}$ + H+ $K=10^{+0.85}$
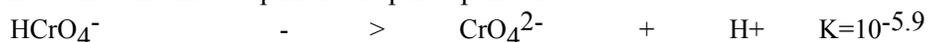
CrO_3

pH > 8 CrO_4^{2-} yellow

2-6 $HCrO_4^-$ & $Cr_2O_7^{2-}$ orange-red

<1 $H_2Cr_2O_7$

$Cr(H_2O)_6^{3+}$ -> $Cr(H_2O)_5(OH)^{2+}$ -> $[(H_2O)_4Cr \quad Cr(H_2O)_4]^{4+}$

pK=4
etc.
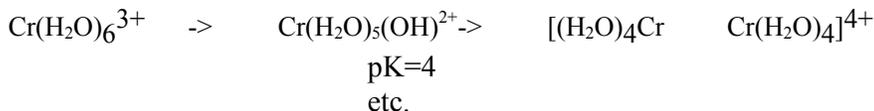
Manganese

	Colour	Oxidation State	MP	
Mn_2O_7	green oil	Mn^{7+}	5.9	
MnO_2	black	Mn^{4+}	535d	
Mn_2O_3	black	Mn^{3+}	1080d	
Mn_3O_4	black	$Mn^{2/3+}$	1705	Haussmanite
MnO	grey-green	Mn^{2+}	1650	

Mn_3O_4 is prepared from the other oxides by heating in air. MnO is prepared from the other oxides by heating with H_2 at temperatures below 1200C

Redox properties of $KMnO_4$.
strong base

MnO_4^-	+	e-	->	MnO_4^{2-}		E=0.56V (RAPID)
$MnO_4^{2-}+2H2O+$		e-	->	$MnO2$ +	4OH-	E=0.60V (SLOW)

moderate base

MnO_4^- +2H2O +		3e-	->	$MnO2$ +	4OH-	E=0.59V

dil. H2SO4

MnO_4^- +8H2O +		5e-	->	Mn^{2+} +	4H2O	E=1.51V
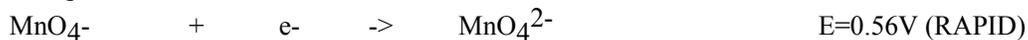
Iron

	Colour	Ox. State	MP	
Fe_2O_3	red brown	Fe^{3+}	1560d	α-form Haematite,
				β-form used in cassettes
Fe_3O_4	black	$Fe^{2/3+}$	1538d	magnetite/lodestone
FeO	black	Fe^{2+}	1380	pyrophoric

α-Fe_2O_3 is obtained by heating alkaline solutions of Fe(III) and dehydrating the solid formed.

FeO,Fe_3O_4,γ-Fe_2O_3	ccp
α-Fe_2O_3	hcp

The Fe(III) ion is strongly acidic:

$Fe(H_2O)_6^{3+}$	+	H_2O	->	$Fe(H_2O)_5(OH)^{2+}$	+	H_3O^+	$K=10^{-3.05}$
$[Fe(OH)(H_2O)_5]^{2+}$	+H_2O	->		$[Fe(OH)_2(H_2O)_4]^+$	+	H_3O^+	$K=10^{-3.26}$

olation

$2Fe(H_2O)_6^{3+}$	+	$2H_2O$	->	$[Fe_2(OH)_2(H_2O)_8]^{4+}$	+	$2H_3O^+$	$K=10^{-2.91}$
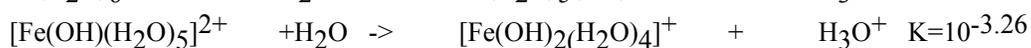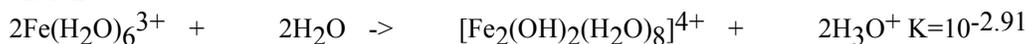
The Fe2+ ion is barely acidic:

$Fe(H_2O)_6^{2+}$	+	H_2O	->	$[Fe(OH)(H_2O)_5]^+$	+	H_3O^+	$K=10^{-9.5}$

The Redox chemistry of Iron is pH dependent:

$$Fe(H_2O)_6^{3+} \quad + \quad e^- \quad \rightarrow \quad Fe(H_2O)_6^{2+}$$
$$E = 0.771V$$
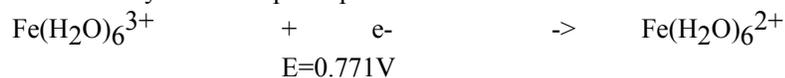
$E = E - RT/nF \; Ln[Fe^{2+}]/[Fe^{3+}]$
at precipitation
$[Fe^{2+}].[OH^-]2 \sim 10^{-14}$
$[Fe^{3+}].[OH^-]3 \sim 10^{-36}$

or for $OH^- = 1M$ then $[Fe^{2+}]/[Fe^{3+}] = 10^{22}$

$$E = 0.771 - 0.05916 \log_{10}(10^{22})$$
$$= 0.771 - 1.301$$
$$= -0.530v$$

thus in base the value of E is reversed and the susceptibility of Fe^{2+} to oxidation increased. In base it is a good reducing agent and will reduce Cu(II) to Cu(0) etc. Note the implications for rust treatment.

Cobalt

	Colour	Oxidation State	MP	Structure
Co_2O_3		Co^{3+}		
Co_3O_4	black	$Co^{2+/3+}$	900-950d	normal spinel
CoO	olive green	Co^{2+}	1795 -antiferromag. < 289 K	NaCl

Co_2O_3 is formed from oxidation of $Co(OH)_2$.
CoO when heated at 600-700 converts to Co_3O_4
Co_3O_4 when heated at 900-950 reconverts back to CoO.

no stable $Co(H_2O)_6^{3+}$ or $Co(OH)_3$ exist.
$Co(H_2O)_6^{2+}$ not acidic

Nickel

	Colour	Oxidation State	MP	Structure
NiO	green powder	Ni^{2+}	1955	NaCl

thermal decomposition of $Ni(OH)_2$, $NiCO_3$, or $NiNO_3$ gives NiO.

Copper

	Colour	Oxidation State	MP
CuO	black	Cu^{2+}	1026d
Cu_2O	red	Cu^+	1230

Cu_2O is prepared from thermal decomposition of $CuCO_3$, $Cu(NO_3)_2$ or $Cu(OH)_2$. The Fehling's test for reducing sugars also gives rise to red Cu_2O. It is claimed that 1mg of dextrose produces sufficient red colour for a positive test.

$Cu(H2O)_6^{2+}$ not acidic

The Redox chemistry of Copper:

$$
\begin{array}{lllll}
Cu^{2+} & + & e- & -> & Cu+ & E=0.15V \\
Cu^{+} & + & e- & -> & Cu & E=0.52V \\
Cu^{2+} & + & 2e- & -> & Cu & E=0.34V \\
\end{array}
$$

By consideration of this data, it will be seen that any oxidant strong enough to covert Cu to Cu^+ is more than strong enough to convert Cu^+ to Cu^{2+} (0.52 cf 0.14V). It is not expected therefore that any stable Cu^+ salts will exist in aqueous solution.
Disproportionation can also occur:

$$2Cu^{+} \quad -> \quad Cu^{2+} \quad + \quad Cu \qquad E=0.37V \text{ or } K=10^6$$
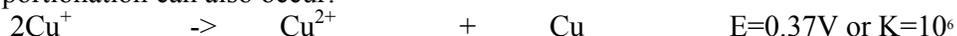
Representative Coordination Complexes

Titanium

$TiCl_4$ is a good Lewis acid and forms adducts on reaction with Lewis bases such as;

$$
\begin{array}{lll}
2PEt_3 & -> & TiCl_4(PEt_3)_2 \\
2MeCN & -> & TiCl_4(MeCN)_2 \\
bipy & -> & TiCl_4(bipy) \\
\end{array}
$$

Solvolysis can occur if ionisable protons are present in the ligand;

$$
\begin{array}{lllll}
2NH_3 & -> & TiCl_2(NH_2)_2 & + & 2HCl \\
4H_2O & -> & TiO_2.aq & + & 4HCl \\
2EtOH & -> & TiCl_2(OEt)_2 & + & 2HCl \\
\end{array}
$$
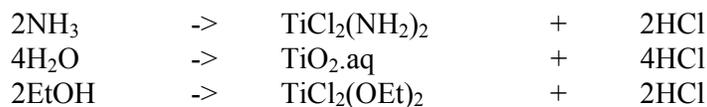
$TiCl_3$ has less Lewis acid strength but can form adducts also;

$$3pyr \qquad -> \qquad TiCl_3pyr_3$$

Vanadium

The Vanadyl ion (eg. from $VO(H_2O)_4SO_4$) retains the V=O bond when forming complexes.

$$VO^{2+} \; + \quad 2acac \qquad -> \qquad VO(acac)_2$$

Vanadyl complexes are often 5 coordinate square pyramidal and are therefore coordinately unsaturated. They can take up another ligand to become octahedral, eg;

$$VO(acac)_2 \quad + \quad pyr \quad -> \quad VO(acac)_2pyr$$

The V=O stretching frequency in the IR can be monitored to see the changes occurring during these reactions. It generally is found at 985 cm-1 but will shift to lower wavenumbers when 6-coordinate, since the bond becomes weaker.

Chromium

The Chromium(III) ion forms many stable complexes which being inert are capable of exhibiting various types of isomerism.

"$CrCl_3.6H_2O$" exists as hydrate isomers, including:

$$trans-[Cr(H_2O)_4Cl_2]Cl.2H_2O \text{ etc}$$

$CrCl_3$ anhydrous reacts with pyridine only in the presence of Zinc powder. This allows a small amount of Cr(II) to be formed, which is very labile.

$$CrCl_3 \quad + \quad pyr/Zn \rightarrow \quad CrCl_3pyr_3$$

$Cr_2(OAc)_4.2H_2O$ is an example of a Cr(II) complex which is reasonably stable in air once isolated. Each Cr(II) ion has 4 d electrons but the complex is found to be diamagnetic which is explained by the formation of a quadruple bond between the two metal ions. The Cr-Cr bond distance in a range of these quadruply bonded species has been found to vary between 195-255 pm.

Manganese

Octahedral complexes of Mn(III) are expected to show J-T distortions. It was of interest therefore to compare the structures of $Cr(acac)_3$ with $Mn(acac)_3$ since the Cr(III) ion is expected to give a regular octahedral shape. In fact the Mn-O bond distances were all found to be equivalent.

An unusual Mn complex is obtained by the reaction of $Mn(OAc)_2$ with KMnO4 in HOAc. This gives $[MnO(OAc)_6 \ 3H_2O]$ OAc. It is used as an industrial oxidant for the conversion of toluene to phenol.

Iron

An important Fe complex which is used in Actinometry since it is photosensitive is $K_3[Fe(C_2O_4)_3.3H_2O$.
It can be prepared from:
$Fe(C_2O_4)$ in $K_2C_2O_4$ by reacting with H_2O_2 in $H_2C_2O_4$ to give green crystals. It is high spin $\mu=5.9$ BM at 300K and has been resolved into its two optical isomers, although they racemise in less than 1 hour.

In light the reaction is:

$$K_3Fe(C_2O_4)_3.3H_2O \quad \rightarrow \quad 2Fe(C_2O_4) \quad + \quad 2CO_2 \quad + \quad 3K_2C_2O_4$$

Another important complex is used as a redox indicator since the Fe(II) and Fe(III) complexes are both quite stable and have different colours:

$$Fe(phen)_3{}^{3+} \quad + \quad e- \quad \rightarrow \quad Fe(phen)_3{}^{2+} \quad\quad E=1.12V$$

     blue   red

      The ligand is 1,10 phenanthroline and the indicator is called ferroin.

Cobalt

The Cobalt(III) ion forms many stable complexes, which being inert, are capable of exhibiting various types of isomerism. The preparation and characterisation of many of these complexes dates back to the pioneering work of Werner and his students. Coordination theory was developed on the basis of studies of complexes of the type:

$[Co(NH_3)_6]Cl_3$ yellow

$[Co(NH_3)_5Cl]Cl_2$ red

trans-$[Co(NH_3)_4Cl_2]Cl$ green

cis-$[Co(NH_3)_4Cl_2]Cl$ purple

etc.

Another important complex in the history of coordination chemistry is HEXOL. This was the first complex that could be resolved into its optical isomers that did not contain Carbon atoms. Since then, only three or four others have been found.

An interesting complex which takes up O_2 from the air reversibly is Cosalen. This has been used as an emergency oxygen carrier in jet aircraft.

Nickel

The Nickel(II) ion forms many stable complexes. Whilst there are no other important oxidation states to consider the Ni(II) ion can exist in a wide variety of CN's which complicates its coordination chemistry.
For example,

for CN=4 both tetrahedral and square planar complexes can be found.

for CN=5 both square pyramid and trigonal bipyramid complexes are formed.

The phrase "anomalous nickel" has been used to describe this behaviour and the fact that equilibria often exist between these forms.

Some examples include:

(a) addition of ligands to square planar complexes to give 5 or 6 coordinate species

(b) monomer/polymer equilibria

(c) square-planar/ tetrahedron equilibria

(d) trigonal-bipyramid/ square pyramid equilibria.

(a) substituted acacs react with Ni^{2+} to give green dihydrates (6 Coord) by heating the waters are removed to give tetrahedral species. The unsubstituted acac complex, Ni(acac)$_2$ normally exists as a trimer, see below.
Lifschitz salts containing substituted ethylenediamines can be isolated as either 4 or 6 coordinate species depending on the presence of coordinated solvent.

(b) Ni(acac)$_2$ is only found to be monomeric at temperatures around 200C in non-coordinating solvents such as n-decane. 6-coordinate monomeric species are formed at room temperature in solvents such as pyridine but in the solid state Ni(acac)$_2$ is a trimer, where each Ni atom is 6-coordinate. Note that Co(acac)$_2$ actually exists as a tetramer.

(c) Complexes of the type NiL_2X_2 where L are phosphines can give rise to either tetrahedral or square planar complexes. It has been found that:

        L=P(aryl)$_3$ are tetrahedral
        L=P(alkyl)$_3$ are square planar
        L=mixed aryl and alkyl phosphines, both stereochemistries can occur in the same crystalline substance.

The energy of activation for conversion of one form to the other has been found to be around 50kJ mol^{-1}.

Similar changes have been observed with variation of the X group:

Ni(PØ$_3$)$_2$Cl$_2$	green tetrahedral	μ =2.83 BM
Ni(PØ$_3$)$_2$(SCN)$_2$	red sq. planar	μ =0.

Ni^{2+} reacts with CN- to give $Ni(CN)_2.nH_2O$ (blue-green) which on heating at 180-200 is dehydrated to yield $Ni(CN)_2$. Reaction with excess KCN gives $K_2Ni(CN)_4.H_2O$ (orange crystals) which can be dehydrated at 100C. Addition of strong concentrations of KCN produces red solutions of $Ni(CN)_5^{3-}$.

The crystal structure of the double salt prepared by addition of $Cr(en)_3^{3+}$ to $Ni(CN)_5^{3-}$ showed that two types of Ni stereochemistry were present in the crystals in approximately equal proportions.

        50% as square pyramid   50% as trigonal bipyramid.

Copper

The Copper(II) ion forms many stable complexes which are invariably described as either 4 coordinate or distorted 6 coordinate species.

$Cu(OH)_2$ reacts with NH_3 to give a solution which will dissolve cellulose. This is exploited in the industrial preparation of Rayon. The solutions contain tetrammines and pentammines. With pyridine, only tetramines are formed eg $Cu(py)_4SO_4$.

A useful reagent for the analytical determination of Cu^{2+} is the sodium salt of N, N-diethyldithiocarbamate. In dilute alcohol solutions, the presence of trace levels of Cu^{2+} is indicated by a yellow colour which can be measured by a spectrometer and the concentration determined from a Beer's Law plot. The complex is $Cu(Et_2dtc)_2$ which can be isolated as a brown solid.

Tutorial Paper #1

1) Give the electronic configuration for the following metal ions in:
   i) Octahedral (high spin)
   ii) Tetrahedral crystal fields

Ti(III), Cu(II), Ni(II), Fe(III), Co(III), Cr(III), V(II), Mn(III), Fe(II), Co(II).

Ans

i) t_{2g}^{1}, t_{2g}^{6} e_{g}^{3}, t_{2g}^{6} e_{g}^{2}, t_{2g}^{3} e_{g}^{2}, t_{2g}^{4} e_{g}^{2}, t_{2g}^{3}, t_{2g}^{3}, t_{2g}^{3} e_{g}^{1}, t_{2g}^{4} e_{g}^{2}, $t_{2g}5$ e_{g}^{2}.

ii) e^{1}, e^{4} t_{2}^{5}, e^{4} t_{2}^{4}, e^{2} t_{2}^{3}, e^{3} t_{2}^{3}, e^{2} t_{2}^{1}, e^{2} t_{2}^{1}, e^{2} t_{2}^{2}, e^{3} t_{2}^{3}, e^{4} t_{2}^{3}.

2) Calculate the crystal field stabilisation energies associated with the following metal ions in both octahedral and tetrahedral crystal fields. Cu(II), Fe(III), Co(II), Co(III), Cr(III), Mn(III).

Ans

Cu(II) d^{9} oct -3/5 Δ(oct) tet -2/5 Δ(tet); Fe(III) d^{5} oct 0 tet 0

Co(II) d^{7} oct -4/5 Δ(oct) tet -6/5 Δ(tet); Co(III) d^{6} oct -2/5 Δ(oct) tet -3/5 Δ(tet)

Cr(III) d^{3} oct -6/5 Δ(oct)-4/5 tet Δ(tet); Mn(III) d^{4} oct -3/5 Δ(oct) tet -2/5 Δ(tet)

3) Draw a graph of the Octahedral Site Preference Energies for high spin d^{5}-d^{10} electron configurations.

4) Briefly explain why Fe_3O_4 adopts the inverse spinel structure, while Mn_3O_4 is normal.
What structures would you expect for $FeCr_2O_4$ and Co_3O_4 ?

5) What is the Irving-Williams series and how can it be rationalised in terms of Crystal Field Theory.

6) Determine the ground state terms for the following configurations d^{3}, d^{6}, d^{5}

7) The absorbance of a 0.1 M aqueous solution of $[Ti(H_2O)_6]^{3+}$ was found to be 0.56 when measured in a 1 cm cuvette. A distorted absorption band was centered at 20,300 cm^{-1}. Account for the spectrum and calculate the molar absorbance (ε). What would be the absorbance of the same solution in a 2 cm cuvette?

8) Predict the electronic spectrum of $[Cr(H_2O)_6]^{2+}$.

9) Comment on the observation that solutions of $MnSO_4$. $7H_2O$ are colourless.

10) The electronic absorption spectrum of $[Ni(H_2O)_6]^{2+}$ shows three bands at 8,500, 15,400 and 26,000 cm^{-1}. Account for these bands using an Orgel diagram.

Tutorial Paper #2

1) Calculate the energy gap between two bands observed at:
  i) 600nm and 500nm
  ii) 500nm and 400nm.

2) What are the ground state terms of the following ions?
a) Ti(II) b) Cr(V) c) Mn(II) d) Fe(II) e) Co(II)

3) Assign the frequencies given below to appropriate d-d transitions.
Calculate Δ (10Dq) for each case.

Ion	$\nu 1$	$\nu 2$	$\nu 3$
$[Cr(H_2O)_6]^{2+}$	14,000		
$[V(H_2O)_6]^{2+}$	12,350	18,500	27,900 cm^{-1}
$[V(H_2O)_6]^{3+}$	17,800	25,700	?

4) To what does the Racah parameter B refer and what factors determine its magnitude?

5) Give the relevant selection rules for electronic transitions in high spin first row transition metal complexes. What factors can lead to their violation?

6) What is the difference between the spectrochemical series and the nephelauxetic series? How were these series established and how do they suggest that there are deficiencies in Crystal Field Theory?

7) How does spin orbit coupling affect:
  i) the magnetic moments of complexes with A or E ground states.
  ii) the magnetic moments of complexes with T ground states?

8) Interpret the following room temperature (300K) magnetic moments.

i) Fe(acac)$_3$ 5.92BM   ii) Mn(acac)$_3$ 4.86BM
iii) BaMnF$_6$ 3.80BM   iv) Cs$_2$CoCl$_4$ 4.71BM
v) K$_2$Cu(SO$_4$)2.6H$_2$O 1.91BM   vi) [Cr(en)$_3$]I$_3$.H2O 3.93BM
vii) VCl$_4$ 1.69BM   viii) K$_4$[Mn(oxalate)$_3$].3H$_2$O 3.18BM
ix) [Ni(NH$_3$)$_6$]Cl$_2$ 3.11BM   x) [Cu(NH$_3$)$_4$](NO$_3$)$_2$ 1.89BM

Tutorial Paper 3

1) Arrange the first row transition metal elements in order of increasing abundance in the Earth's crust.

2) Describe the extraction of Ti, Fe, Ni.

3) Write the electronic configuration of Cu(I), Cr(II), Ti(III), Mn(II), Ni(III) and Co(II).

4) What is the Jahn-Teller theorem and what are Jahn-Teller distortions?

5) Write the electronic configurations for those ions expected to show Jahn-Teller distortions.

6) Discuss the structure of VF_5 in the solid, liquid and gas phases.

7) Give the structure and method of preparation of basic manganese(III) acetate.

8) How is cobalt(III) fluoride prepared? Account for the lack of all other Co(III) halides.

9) Why is it difficult to obtain Cu(I) species in aqueous solution?

10) What happens when:
    a) solid potassium manganate(VII) is added to conc. HCl?
    b) potassium manganate(VII) is used as an oxidant under strongly alkaline conditions?

11) Many compounds of the type MX_2 (where X=F,Cl,Br,I) adopt structures that can be described as: rutile, $CdCl_2$ or CdI_2. Describe these three structures giving examples of first row transition metal halides that adopt them.