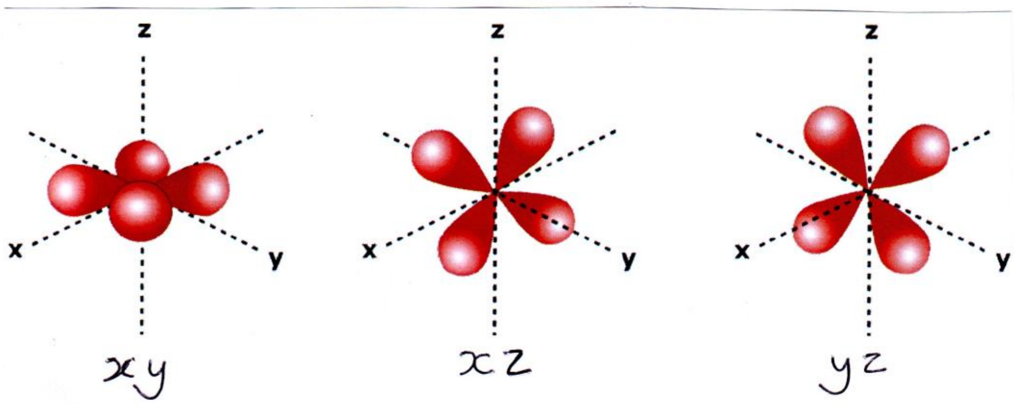
The colour of complexes (A2)

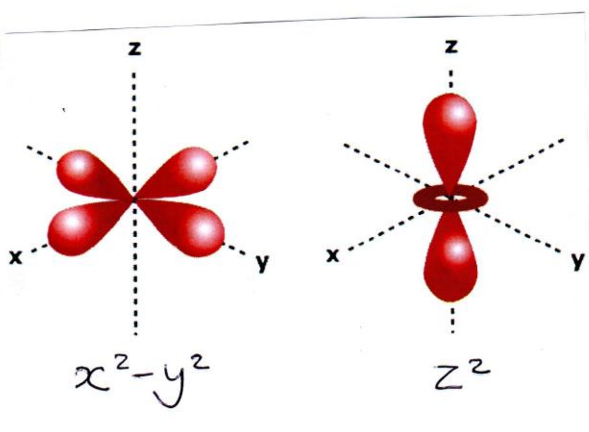
A characteristic of transition metal is their ability to form coloured compounds.

- ions with d^{10} (full), eg. Cu^+, Ag^+, Zn^{2+} or d^0 (empty), eg. Sc^{3+} configuration are colourless.
- eg. titanium (IV) oxide TiO_2 is white.
- ions with partially filled d-orbitals tend to be coloured.
- it is caused by the ease of transition of electrons between energy levels.
- energy is absorbed when an electron is promoted to a higher level.
- white light is made up of all the colours of the visible spectrum.

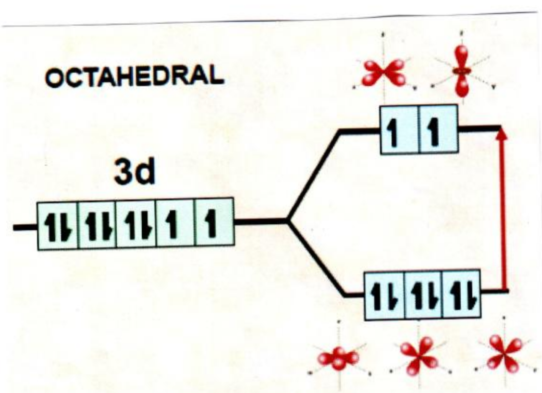
• when a solution containing a transition metal ion in a complex appear coloured, part of the visible spectrum is absorbed by the solution.

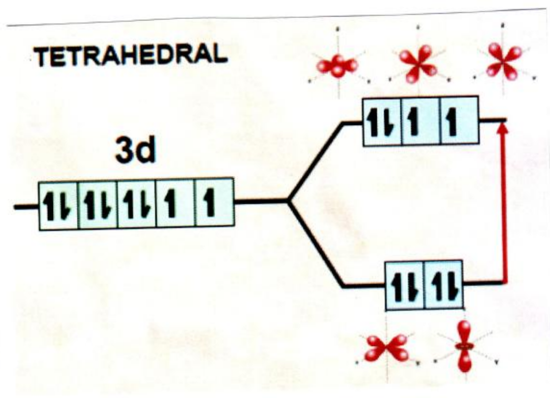
• The degenerate d orbitals in a transition metal atom as follow:



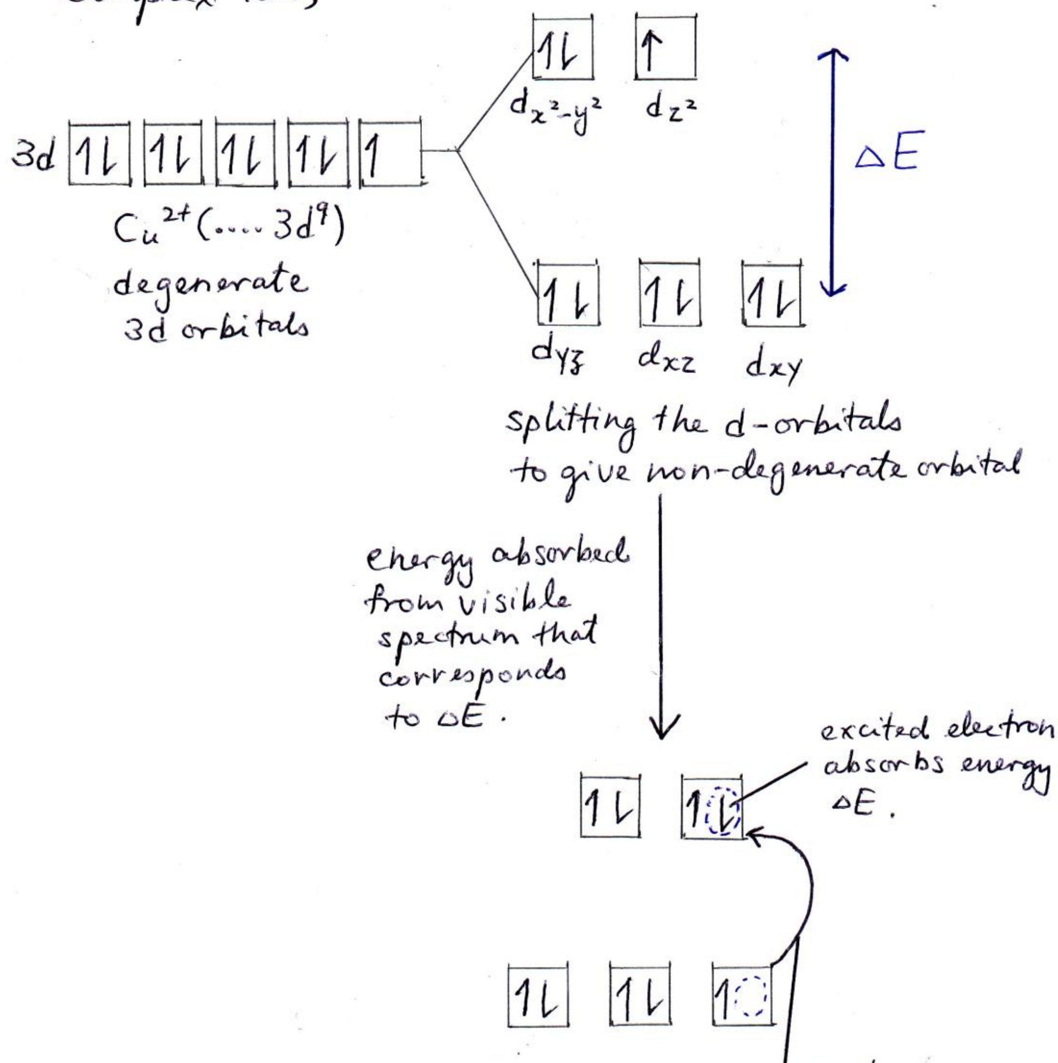


- The five d-orbitals in an isolated transition metal atom or ion are described as degenerate, i.e. they are all at the same energy level.
- In the presence of ligands, a transition metal ion is not isolated.
- the co-ordinate bonding from the ligands causes the 5 d-orbitals in the transition metal ion to split into 2 sets of non-degenerate orbitals at slightly different energy levels.
- in an octahedral complex, two (z^2 and x^2-y^2) go higher and three go lower.
- in a tetrahedral complex, three (xy, xz and yz) go higher and two go lower.





• eg. the splitting of the 3d orbitals in a $Cu(H_2O)_6^{2+}$ complex ion,



The energy absorbed can be worked out by the equation:

$$\Delta E = h\nu$$

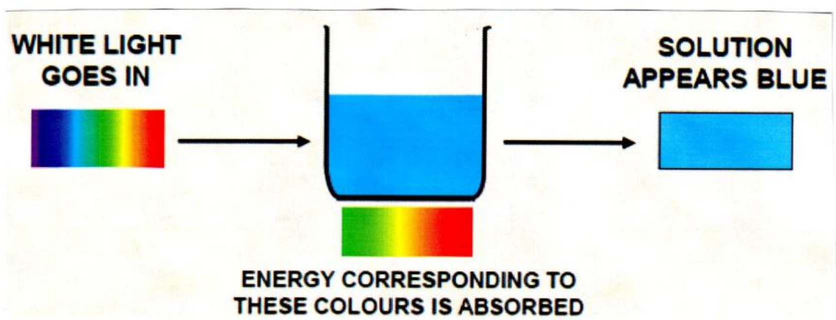
where ν is the frequency of light absorbed
h is planck's constant.

- The lone pairs (used in dative bonds) from the ligands bonded to the transition metal ion repel electrons in the two $d_{x^2-y^2}$ and d_{z^2} orbitals. (because these d orbitals line up with the co-ordinate bonds in the complex's octahedral shape and so they are closer to the bonding electrons in the octahedral arrangement, increasing repulsion between electrons).
- When light shines on the solution containing the $Cu(H_2O)_6^{2+}$ complex, an electron absorbs this amount of energy ΔE. It uses this energy to jump into the higher of the two non-degenerate energy levels.
- In copper complexes, the rest of the visible spectrum that passes through the solution makes it appear blue in colour.
- The exact energy different (ΔE) between the non-degenerate d orbitals in a transition metal ion is affected by many factors:
  1. the nature of the transition metal ion.
  2. the oxidation state of the transition metal ion.
  3. the nature of the ligands
  4. the co-ordination of the ion.

Coloured ions

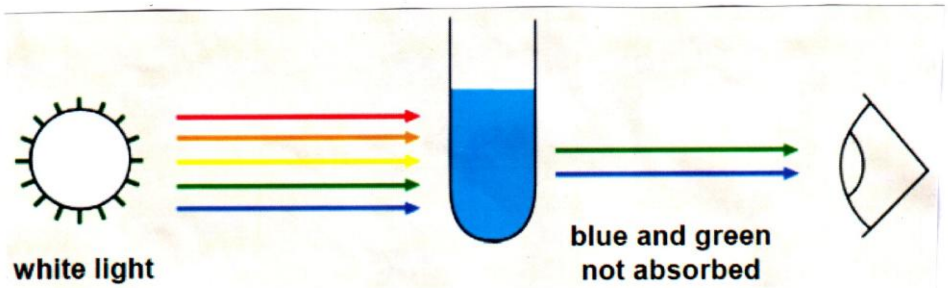
The observed colour of a solution depends on the wavelengths absorbed.

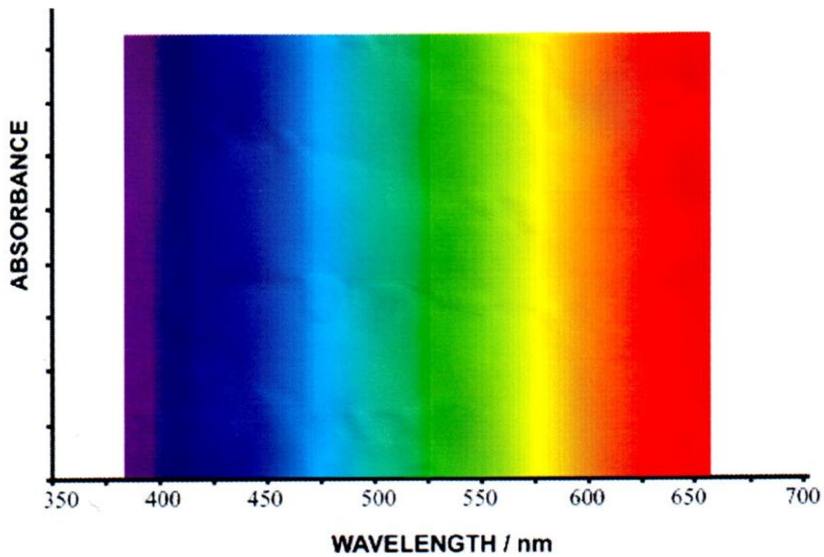
- copper sulfate solution appears blue because the energy absorbed corresponds to red and yellow wavelengths.
- wavelengths corresponding to blue ligth aren't absorbed.

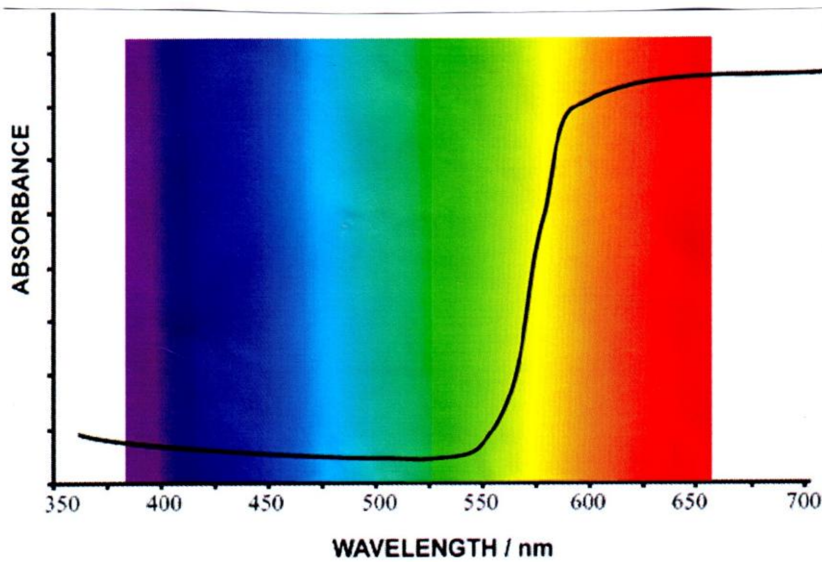


absorbed colour	nm	observed colour	nm
violet	400	green-yellow	560
blue	450	yellow	600
blue-green	490	red	620
yellow-green	570	violet	410
yellow	580	dark blue	430
orange	600	blue	450
red	650	green.	520

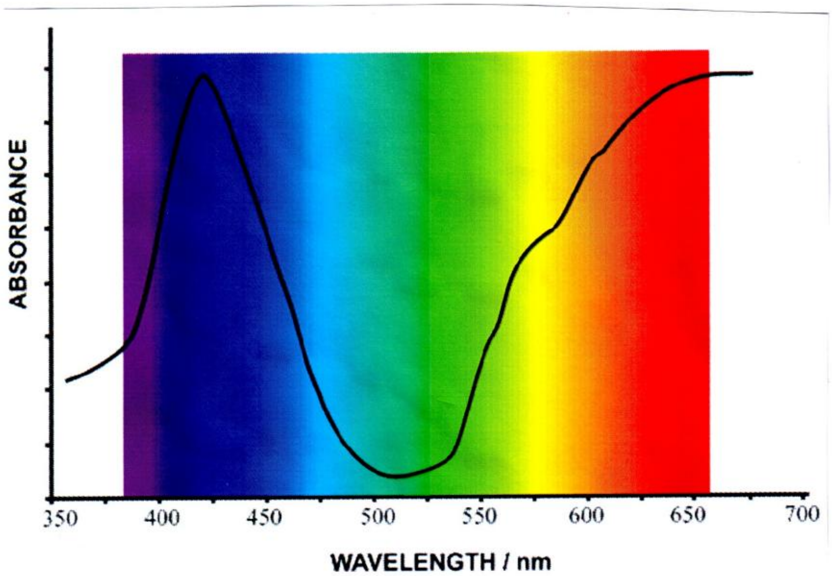
a solution of copper(II) sulfate is blue because red and yellow wavelengths are absorbed.





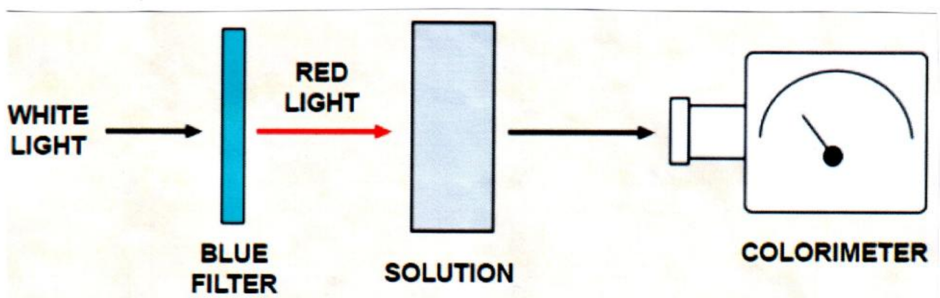


a solution of nickel(II) sulfate is green because violet, blue and red wavelengths are absorbed.



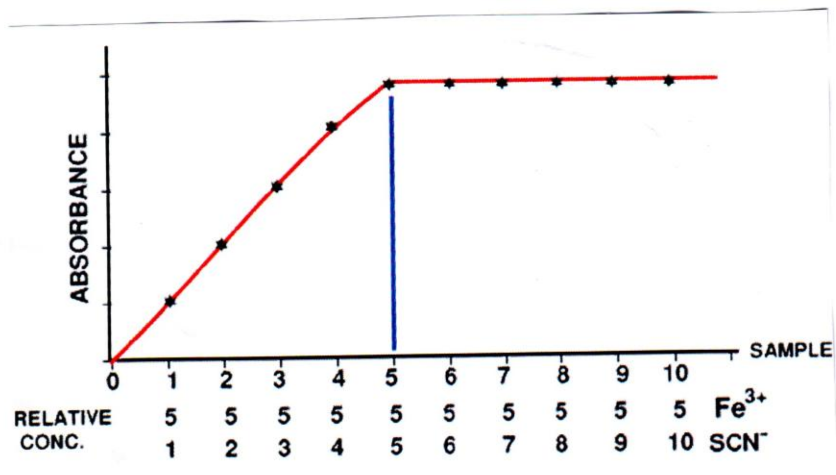
Finding complex ion formula using colorimetry.

- a change of ligand can change the colour of a complex.
- this property can be used to find the formula of a complex ion.
- ligth of a certain wavelength is passed through a solution .
- the greater the colour intensity , the greater the absorbance.
- the concentration of each species in the complex is altered.
- the mixture with the greatest absorbance identifies ratio of ligands and ions.



Example: Finding the formula of an iron(III) complex

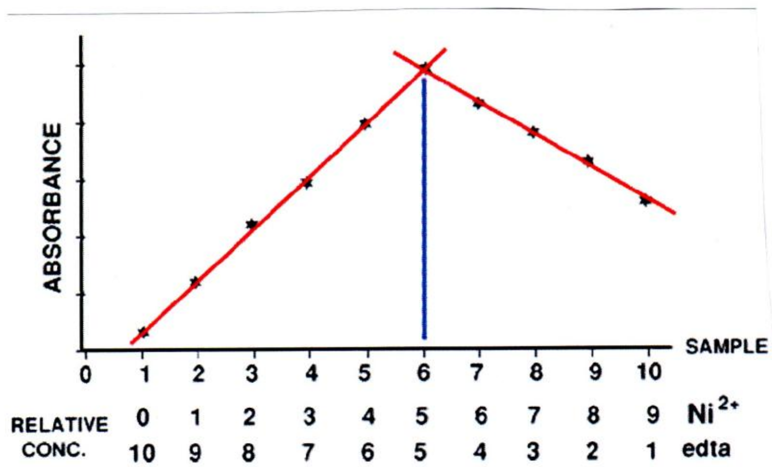
While light is passed through a blue filter.
The resulting red light is passed through mixtures of an aqueous iron(III) and potassium thiocyanate solution.
Maximum absorbance occurs first when the ratio of Fe^{3+} and SCN^- is 1:1.
This shows the complex has the formula
$[Fe(H_2O)_5SCN]^{2+}$



Example: Finding the formula of a nickel(II) edta complex

Filtered light is passed through various mixtures of an aqueous solution of nickel(II) sulfate and edta solution.

The maximum absorbance occurs when the ratio of Ni^{2+} and edta is 1:1.



Exercise 1

What do we mean by 'degenerate atomic orbitals'?

Workings

Orbitals at the same energy level.

Exercise 2

Explain why an **octahedral** complex of a transition element is coloured.

Workings

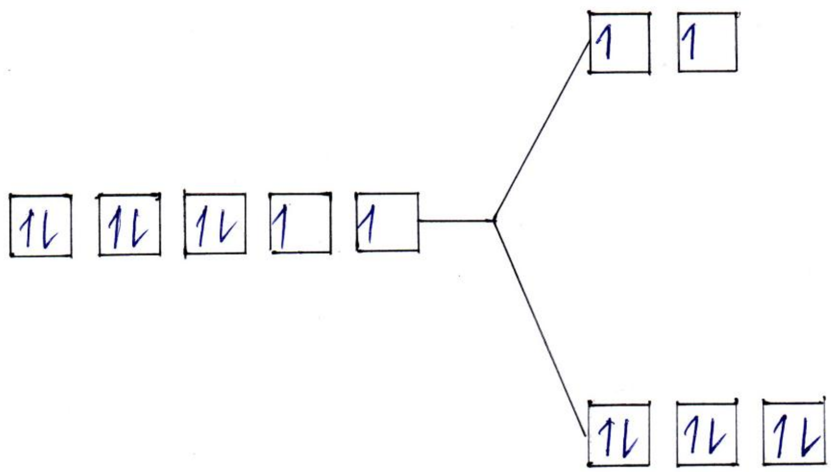
The ligands in a complex cause the d orbitals to split, forming two sets of non-degenerate orbitals.
The difference in the energy (ΔE) between the non-degenerate d orbitals corresponds to the energy of part of the visible spectrum of light.
When light travels through a solution or a solid containing the complex, an electron from one of the three lower non-degenerate orbitals absorbs that amount of energy (ΔE) and jumps into one of the two higher non-degenerate orbitals.
This leaves the transmitted light coloured.

Exercise 3

Draw a diagram to show the non-degenerate 3d orbitals in a Ni^{2+} ion. The electrons should be shown in the configuration that gives the lowest possible energy.

Workings

electronic configuration Ni^{2+} [Ar] $3d^8$



Exercise 4

A solution of Sc^{3+} ions is colourless.
Suggest a reason for this.

Workings

Sc^{3+} ions have electronic configuration [Ar] $3d^0 4s^0$.
If d-orbital splitting were to occur in a complex ion containing Sc^{3+}, there would be no electron in the three 3d-orbitals of lower energy level, so visible light would not be absorbed in promoting an electron from a lower energy 3d orbital to a higher energy 3d orbital.

Exercise 5

A solution of Zn^{2+} ions is colourless.
Suggest a reason for this.

Workings

Zn^{2+} ions have electronic configuration [Ar] $3d^{10} 4s^0$.
If d-orbital splitting were to occur in a complex ion containing Zn^{2+}, each of the 3d orbitals would contain two electrons, and would therefore be fully occupied.
Visible light could not be absorbed in promoting an electron from a lower energy 3d orbital to a higher energy 3d orbital.