

# Kirkcaldy High School



## Chemistry

### Advanced Higher

### Unit 1 - Inorganic Chemistry

## NOTES

# Course Overview

## Contents

The Advanced Higher Chemistry Course is split into four units. *Italic* shows the contents of this notes booklet.

### **Unit 1 - Inorganic Chemistry**

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- (b) Atomic orbitals, electronic configurations and the periodic table* *page 10*
- (c) Transition Metals* *page 26*

### **Unit 2 - Physical Chemistry**

- (a) Chemical Equilibrium
- (b) Reaction Feasibility
- (c) Kinetics

### **Unit 3 - Organic Chemistry and Chemical Analysis**

- (a) Molecular Orbitals
- (b) Synthesis
- (c) Stereochemistry
- (d) Experimental Determination of structure
- (e) Pharmaceutical Chemistry

## Unit 4 - Researching Chemistry

- (a) Weighing by difference and gravimetric analysis
- (b) Preparing a standard
- (c) Using a reference or control or blank determination
- (d) Carrying out a complexometric titration
- (e) Carrying out a back titration
- (f) Using a colorimeter or visible spectrophotometer and carrying out dilution to prepare a calibration graph
- (g) Distilling
- (h) Refluxing
- (i) Using vacuum filtration methods
- (j) Recrystallising
- (k) Determining % yield experimentally
- (l) Using thin-layer chromatography
- (m) Using melting point apparatus and mixed melting point determination
- (n) Using a separating funnel and solvent extraction
- (o) Carrying out stoichiometric calculations
- (p) Volumetric Analysis
- (q) Scientific Precision and Uncertainties

## Assessment

- There is a final exam for Advanced Higher Chemistry. It lasts for 3 h and contains 110 marks scaled to a total of 120. There are.
  - 25 marks of multiple-choice questions
  - 85 marks of written answer questions
- There is a Project to write for Advanced Higher Chemistry.
  - The Assignment is externally marked by an SQA marker (NOT your teacher)
  - The Assignment contains 25 marks, but these are scaled to 40 marks such that the assignment is worth one quarter of the total marks.
  - You have unlimited time to research and gather data for your Assignment.
  - It must contain data and analysis from experiments you have carried out.

## Success Criteria

No.	Learning Outcome	Understanding?
1	What are electromagnetic waves?	😊 😐 😞
2	What is the relationship between the speed of light, frequency and wavelength?	😊 😐 😞
3	Do particles or waves make up all electromagnetic radiation?	😊 😐 😞
4	How is the energy of a photon calculated, and how can this be done for a mole of atoms releasing photons?	😊 😐 😞
5	How are atomic emission spectra used to provide evidence of energy levels in atoms?	😊 😐 😞
6	What are atomic emission and atomic absorption spectroscopy and how are they used to identify the quantities of elements in a sample?	😊 😐 😞
7	What are quantum numbers and what do they represent?	😊 😐 😞
8	What are the shapes of the s, p, and d orbitals?	😊 😐 😞
9	How do factors such as Hund's Rule, the Aufbau Principle and the Pauli Exclusion Principle determine electronic configuration?	😊 😐 😞
10	How do the sections of the Periodic table relate to which orbitals are being filled in atoms?	😊 😐 😞
11	How does ionisation energy relate to how full orbitals are?	😊 😐 😞
12	How can the filling of shared orbitals be used to predict the shapes of molecules?	😊 😐 😞
13	Why are transition metal compounds often coloured?	😊 😐 😞
14	How do ligands affect the colour in transition metal complexes?	😊 😐 😞
15	How does electronic configuration tell us which transition metals are coloured and which are colourless?	😊 😐 😞

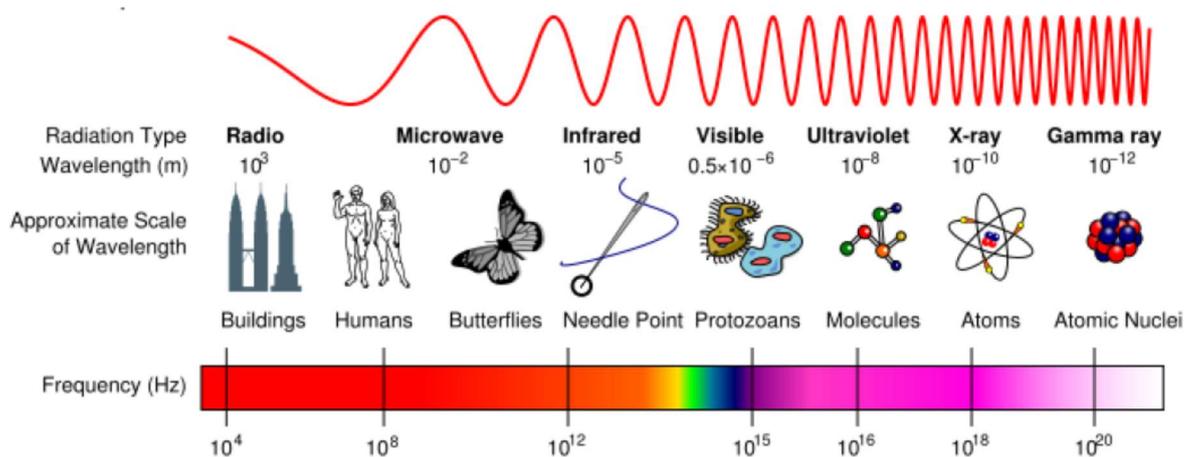
16	What happens to the oxidation number of a transition metal when it is oxidised or reduced?	  
17	What are the rules for naming transition metal complexes?	  
18	How can UV/Visible absorption spectroscopy be used to determine the concentration of coloured compounds in solution?	  

# (a) Electromagnetic radiation and atomic spectra

## Electromagnetic Radiation

Radiation such as light, microwaves, X-rays, television and radio signals is collectively called electromagnetic radiation.

Electromagnetic radiation may be described in terms of waves of varying length between  $10^{-14}$  m and  $10^{+4}$  m that travel in a vacuum at a constant velocity of approximately  $3 \times 10^8$  m s<sup>-1</sup>.



➤ ➤ ➤ Energy Increases and Frequency Increases ➤ ➤ ➤

◀ ◀ ◀ Wavelength Increases ◀ ◀ ◀

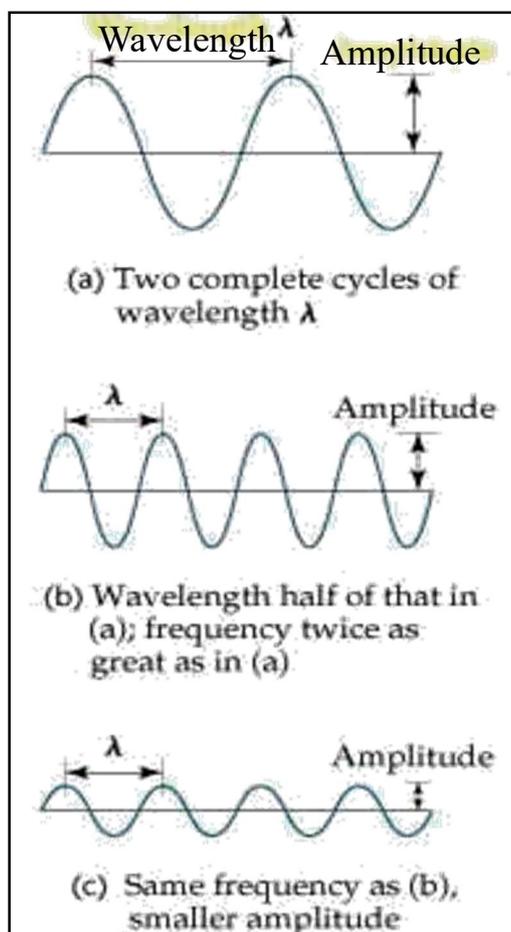
The wavelength of a wave is the distance between adjacent wavecrests or high points (or successive troughs or low points). This distance is measured in metres (m) or an appropriate sub-multiple such as nanometres (nm). A nanometre is  $10^{-9}$  metres. The symbol for wavelength is the Greek letter  $\lambda$  (lambda). All waves have a characteristic **wavelength**  $\lambda$ , measured in metres (m) to nanometres (nm)

The **frequency**,  $f$ , of a wave is the number of waves which pass a point in one second measured in Hertz (Hz) or per seconds (s<sup>-1</sup>)

The **speed** of a wave,  $c$ , is given by its frequency multiplied by its wavelength:

$$c = f\lambda$$

For light,  $c = 3.00 \times 10^8$  ms<sup>-1</sup>



Another unit of 'frequency' used in spectroscopy is the **wavenumber** ( $1/\lambda$ ), measured in  $\text{cm}^{-1}$

Electromagnetic Radiation can also be thought of as a stream of very small particles known as **photons**.

Electromagnetic radiation exhibits wave-particle **dual properties**.

The **energy (E)** of a **photon** (particle) is related to the **frequency** (wave) of the radiation as follows:

$$E = hf$$

where  $h$  is **Planck's constant** ( $6.63 \times 10^{-34} \text{ J s}$ ).

The **energy** calculated would be in Joules (J) and would be a very small quantity.

Normally, we would calculate the energy transferred by the **emission** or **absorption** of **one mole of photons** as follows:

$$E = Lhf \quad \text{or} \quad E = \frac{Lhc}{\lambda}$$

Where  $L$  is the **Avogadro Constant**,  $6.02 \times 10^{23}$  and  $E$  would now be in  $\text{J mol}^{-1}$  or  $\text{kJ mol}^{-1}$ .

### Worked Example

A neon strip light emitted light with a wavelength of 640 nm.

$$640 \text{ nm} = 640 \times 10^{-9} \text{ m} = 6.40 \times 10^{-7} \text{ m.}$$

For each photon:

$$\begin{aligned} E &= \frac{hc}{\lambda} \\ &= \frac{(6.63 \times 10^{-34} \text{ J s}) \times (3.00 \times 10^8 \text{ m s}^{-1})}{6.40 \times 10^{-7} \text{ m}} \\ &= 3.11 \times 10^{-19} \text{ J} \end{aligned}$$

For 1 mole of photons:

$$\begin{aligned} E &= 3.11 \times 10^{-19} \text{ J} \times 6.02 \times 10^{23} \text{ mol}^{-1} \\ &= 1.87 \times 10^5 \text{ J mol}^{-1} \\ &= 187 \text{ kJ mol}^{-1} \end{aligned}$$

## Atomic Spectra

White light produces a continuous spectrum of colour when passed through a prism:



## Emission Spectra

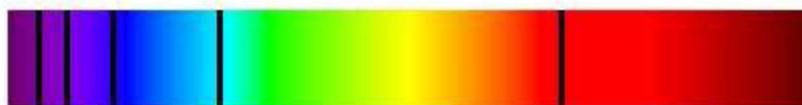
However, if a substance e.g NaCl or H, is burned in a Bunsen flame or discharge tube and the resultant light is passed through a prism, a discontinuous spectrum results:



This spectrum only shows the frequencies of light produced as excited electrons fall back to their original energy levels.

## Absorption Spectra

Passing light through a sample of gas and then through a prism will produce an absorption spectrum, which is missing the frequencies of light absorbed by the atom as electrons are promoted to different energy levels:

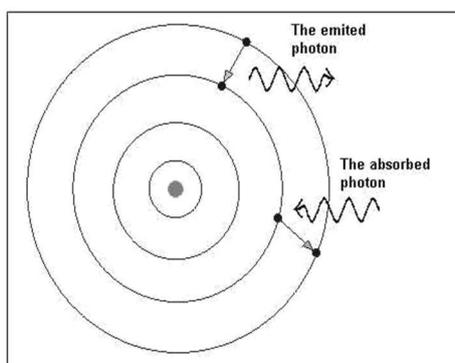


**Atomic emission spectra** provided significant contributions to the modern picture of atomic structure. The spectrum obtained when hydrogen atoms are excited shows four lines: red, blue-green, blue and indigo



**Bohr** deduced that the colours were due to the movement of **electrons** from a higher energy level back to the 'ground state'.

The significance of a Line Spectrum is that it suggests that electrons can only occupy certain **fixed energy levels**.



The electron emits or absorbs the energy changing the orbits.

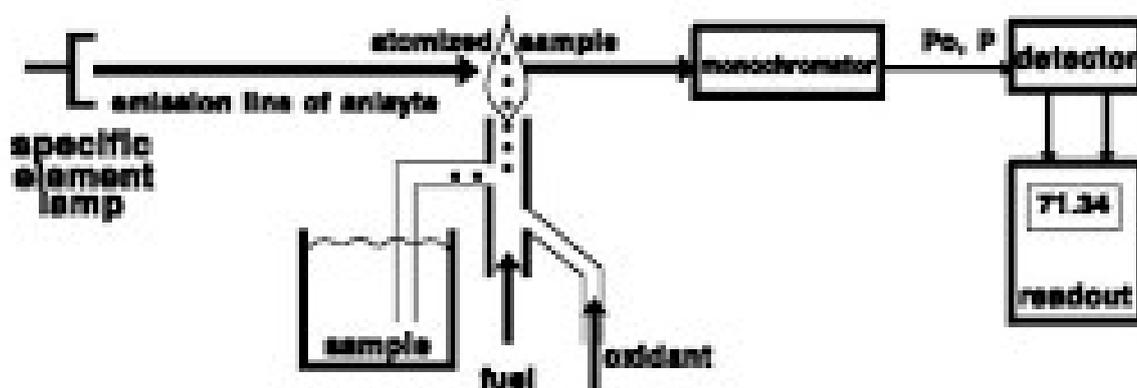
A photon of light is emitted or absorbed when an electron changes from one energy level (shell) to another.

If a blank or reference sample is introduced, it is possible to quantify how much of an element is present in a sample, as the intensity of light absorbed will be proportional to concentration.

$$A \propto C$$

## Atomic Spectroscopy with Flames

### Atomic Absorption Spectroscopy



$P_0$  = light intensity w/ blank  
 $P$  = light intensity w/ sample  
 $A = \log(P_0/P) = kbC$   
 $b$  = flame path;  $C$  = sample concn  
it depends on absorptivity and flow

## (b) Atomic orbitals, electronic configurations and the periodic table

### (i) Quantum Numbers and Hydrogen Emission Spectra

Bohr described each shell by a number, the principal quantum number,  $n$ .

For the first shell,  $n = 1$

For the second shell,  $n = 2$  and so on.

When an electron absorbs energy, it moves from a lower level ( $E_1$ ) to a higher energy level (e.g.  $E_2$ ).

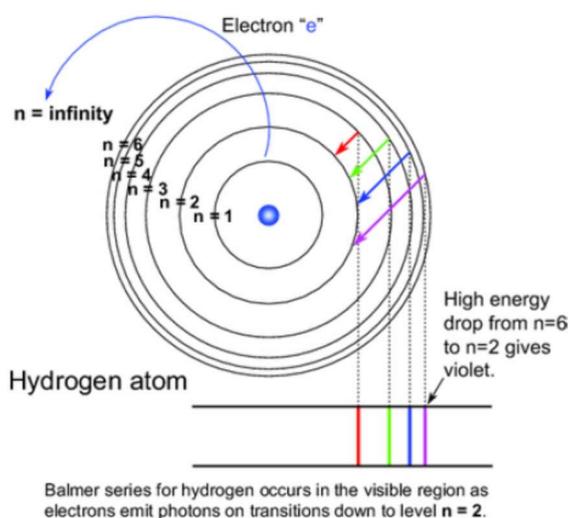
When it drops back, it emits a photon of light with energy:

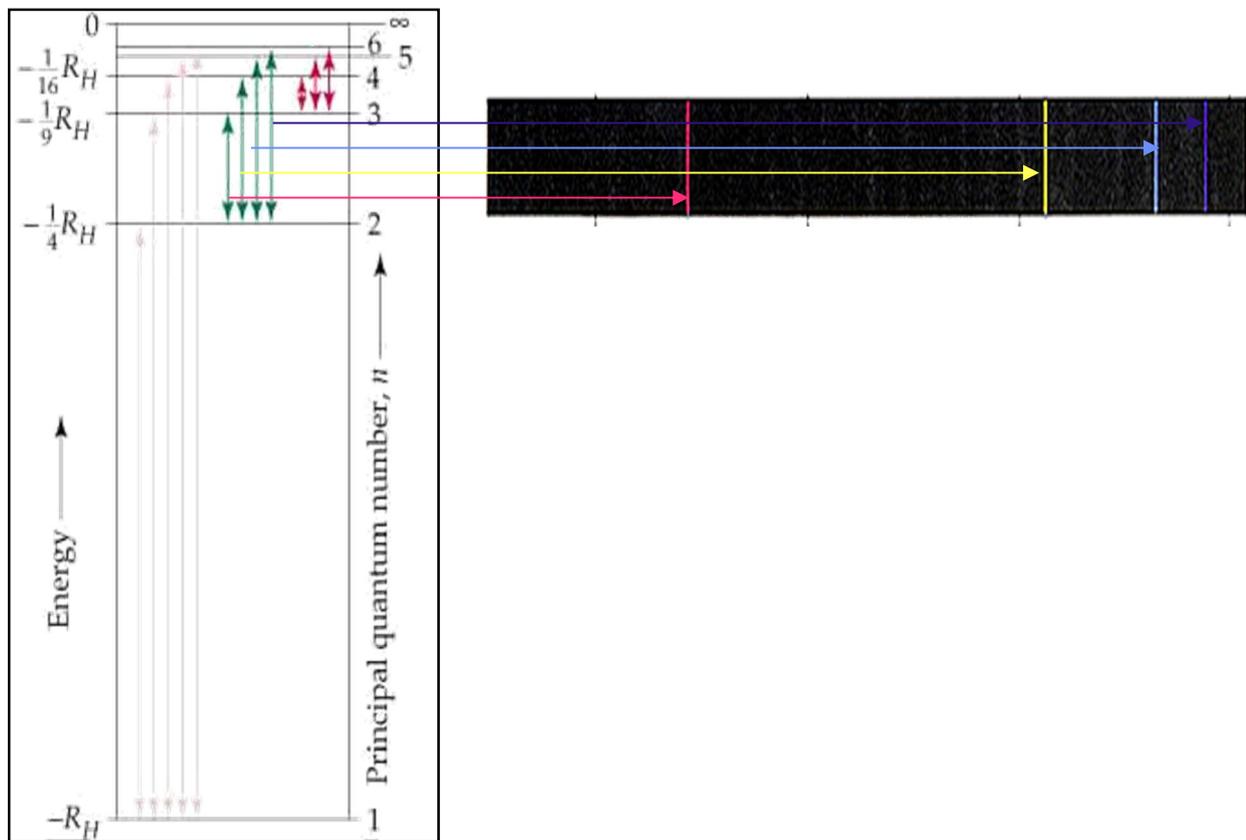
$$\Delta E = E_2 - E_1 = hf$$

After lots of maths, Bohr showed that

$$E_n = -R_H \left( \frac{1}{n^2} \right)$$

where  $n$  is the principal quantum number (i.e.,  $n = 1, 2, 3, \dots$ ), and  $R_H$  is the Rydberg constant =  $2.18 \times 10^{-18}$  J.





The lines detected in the visible spectrum were due to electrons returning to the  $n=2$  level and are called the **Balmer Series**

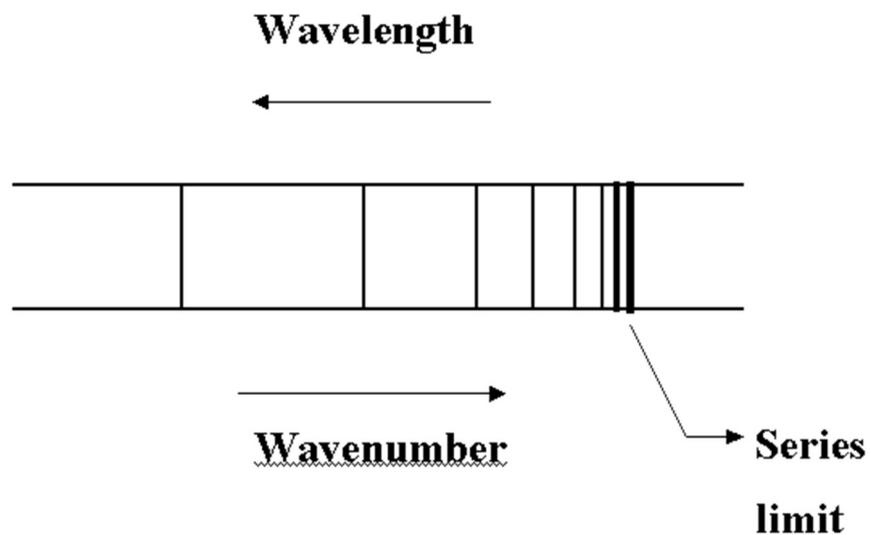
Another series of lines called the **Lyman Series** are due to electrons returning to the  $n=1$  level. The  $\Delta E$  values are higher and the lines appear in the **ultra-violet** region.

### Spectra and Ionisation Energy

When we examine spectra we notice that each series of lines **converge**, i.e the gaps between the lines get smaller and smaller until the lines seem to merge.

The line of greatest energy (lowest wavelength, highest frequency), represents an electron returning from the outer limit of an atom to the ground state ( $n=1$  in the case of Hydrogen).

With slightly more energy the electron would have removed from the atom completely, *i.e.* the **Ionisation Energy**



For example, the wavelength of the line at the convergence limit of the Lyman series in the Hydrogen spectrum is 91.2 nm.

$$91.2 \text{ nm} = 91.2 \times 10^{-9} \text{ m} = 9.12 \times 10^{-8} \text{ m}.$$

For each **photon**:

$$\begin{aligned} E &= \frac{hc}{\lambda} \\ &= \frac{6.63 \times 10^{-34} \times 3.00 \times 10^8}{9.12 \times 10^{-8}} \\ &= 2.18 \times 10^{-18} \text{ J} \end{aligned}$$

For **1 mole of photons**:

$$\begin{aligned} E &= 2.18 \times 10^{-18} \times 6.02 \times 10^{23} \text{ J} \\ &= 1.31 \times 10^6 \text{ J mol}^{-1} \\ &= 1,310 \text{ kJ mol}^{-1} \end{aligned}$$

Check the Data Book to see how close this is to the literature value for ionisation energy!

## More Quantum Numbers

**Angular Quantum Number,  $l$ .** This quantum number describes the **shape** of an orbital.  $l = 0, 1, 2,$  and  $3$  (4 shapes) within each energy level ( $n$ ) but we use letters for  $l$  ( $s, p, d$  and  $f$ ). Usually we refer to the  **$s, p, d$  and  $f$ -orbitals**

Principal Quantum number value $n$	Second Quantum number value: $l$	Sub-shell name
1	0	1s
2	0	2s
	1	2p
3	0	3s
	1	3p
	2	3d

**Magnetic Quantum Number,  $m_l$ .** This quantum number describes the **orientation** of orbitals of the same shape. The magnetic quantum number has integral values between  $-l$  and  $+l$ . However, we use  $p_x, p_y$  and  $p_z$  instead.

Within the appropriate energy levels,

There are **3** possible  $p$ -orbitals                      -1      0      +1

There are **5** possible  $d$ -orbitals            -2      -1      0      +1      +2

There are **7** possible  $f$ -orbitals

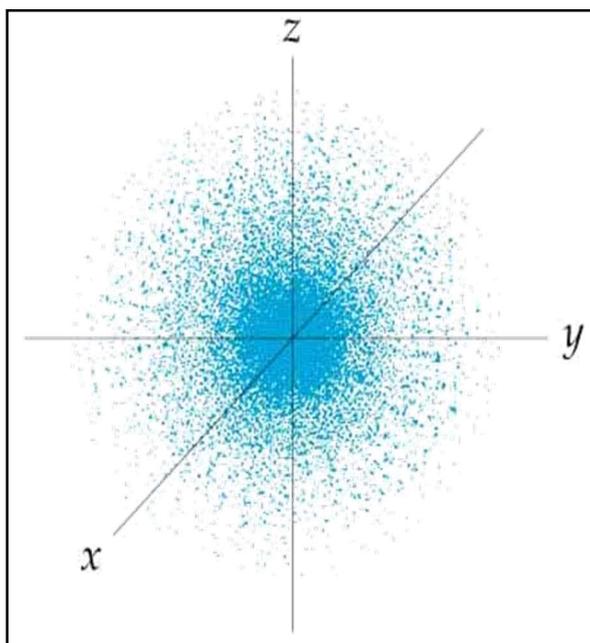
Sub-shell name	Possible value: $l$	Possible value: $m$
1s	0	0
2s	0	0
2p	1	-1, 0, +1
3s	0	0
3p	1	-1, 0, +1
3d	2	-2, -1, 0, +1, +2

Each of the orbitals have different shapes and orientations, which the quantum numbers are used to annotate:

## s-orbital

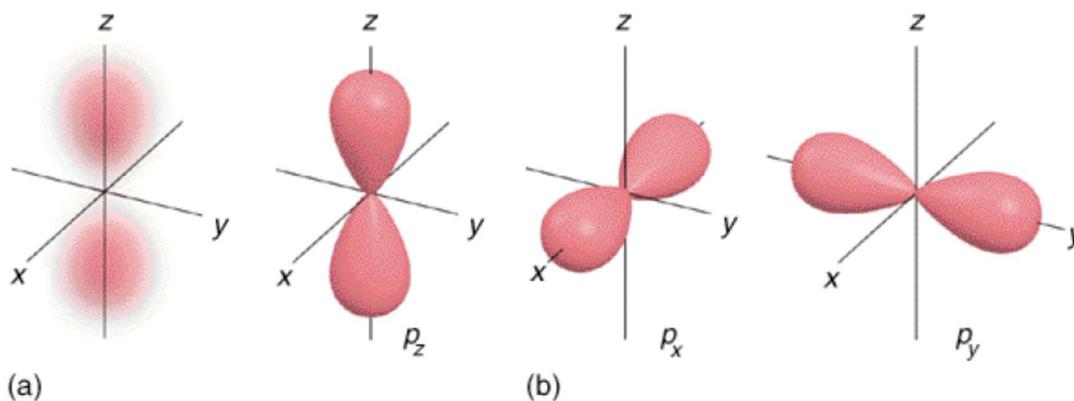
Quantum mechanics has shown that **s orbitals** are **spherical** in shape

An orbital is a **region in space where there is a greater than 90% probability of finding an electron.**



## p-orbitals

The **shape** of a **p-orbital** is **dumb-bell**, ( $l = 1$ ).



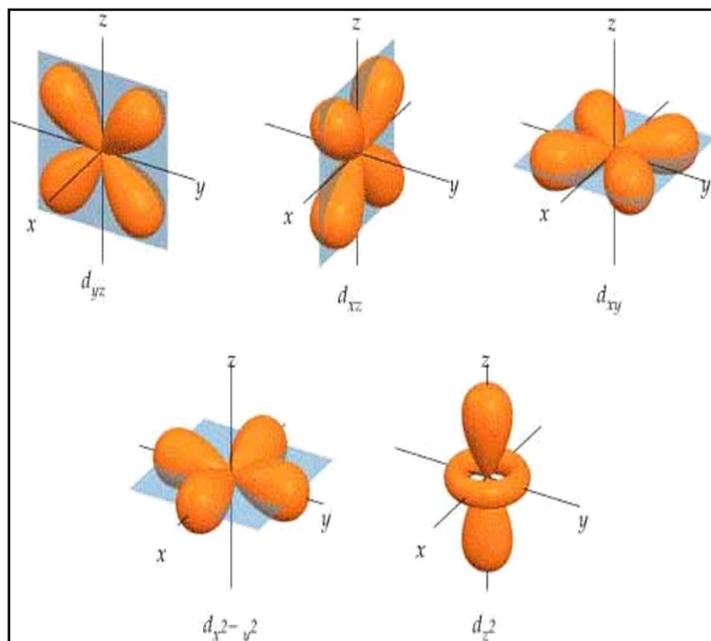
Each shell, from the second shell onwards, contains **three** of these **p-orbitals**, ( $m_l = -1 \ 0 \ +1$ ).

We describe their **orientation** as 'along the x-axis',  $p_x$  'along the y-axis',  $p_y$  and 'along the z-axis',  $p_z$

## d-orbitals

The **shape** of **d-orbitals** ( $l = 2$ ) are more complicated.

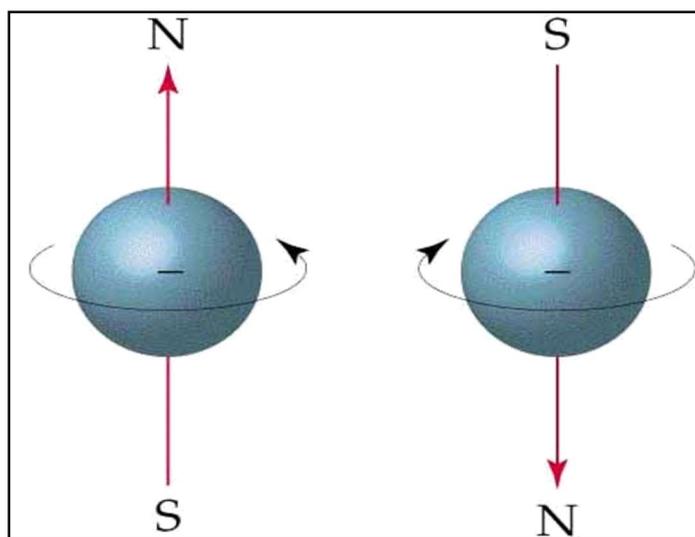
Each shell, from the third shell onwards, contains **five** of these **d-orbitals**, ( $m_l = -2 \ -1 \ 0 \ +1 \ +2$ ).



We describe their orientation as :

‘between the x-and y-axis’,  $d_{xy}$ , ‘between the x-and z-axis’,  $d_{xz}$ , ‘between the y-and z-axis’,  $d_{yz}$ , ‘along the x- and y-axis’,  $d_{x^2-y^2}$  and ‘along the z-axis’,  $d_{z^2}$

**Spin Quantum Number,  $m_s$ :** Each orbital can hold up to 2 electrons. In 1920 it was realised that an electron behaves as if it has a spin. A fourth quantum number was needed.



The spin quantum number,  $m_s$  only has two values  $+1/2$  and  $-1/2$ .

Therefore, up to four quantum numbers,  $n$  (shell),  $l$  (shape),  $m_l$  (orientation) and  $m_s$  (spin) are needed to uniquely describe every electron in an atom.

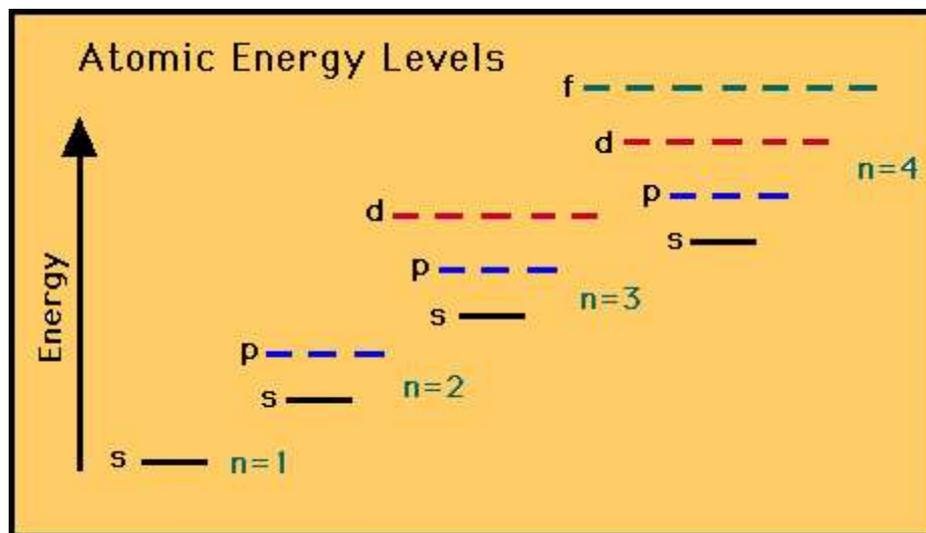
## Electron Configuration

There are 3 rules which determine in which orbitals the electrons of an element are located. The Aufbau Principle states that electrons will fill orbitals starting with the orbital of lowest energy. For degenerate orbitals, electrons fill each orbital singly before any orbital gets a second electron (Hund’s Rule of Maximum Multiplicity).

The Pauli Exclusion Principle states that the maximum number of electrons in any atomic orbital is two and if there are two electrons in an orbital they must have opposite spins (rather than parallel spins).

Orbitals can be ranked in terms of energy to yield an Aufbau diagram. As  $n$  increases, note that the spacing between energy levels becomes smaller. Sets, such as the  $2p$ -orbitals, are of equal energy, they are degenerate

Notice that the third and fourth shells overlap



When writing an electron configuration, the orbitals must be filled with electrons in the order of their energies:

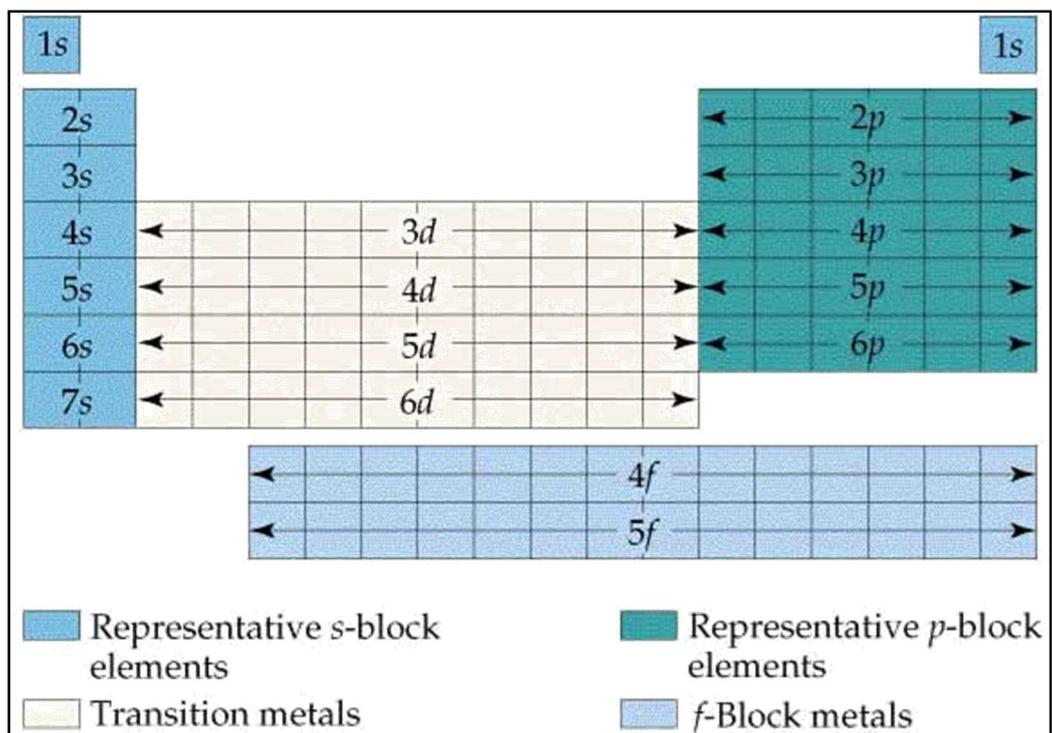
Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram				Electron Configuration
		1s	2s	2p	3s	
Li	3	$\uparrow\downarrow$	$\uparrow$	$\square$ $\square$ $\square$	$\square$	$1s^2 2s^1$
Be	4	$\uparrow\downarrow$	$\uparrow\downarrow$	$\square$ $\square$ $\square$	$\square$	$1s^2 2s^2$
B	5	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $\square$ $\square$	$\square$	$1s^2 2s^2 2p^1$
C	6	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $\uparrow$ $\square$	$\square$	$1s^2 2s^2 2p^2$
N	7	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $\uparrow$ $\uparrow$	$\square$	$1s^2 2s^2 2p^3$
Ne	10	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\square$	$1s^2 2s^2 2p^6$
---	11	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow$	$1s^2 2s^2 2p^6 3s^1$

Cu and Cr are exceptions to this rule - see later section on transition metals.

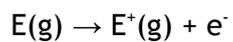
## The Periodic Table

The elements in the periodic table are blocked according to which orbitals are being filled in the atom.



## Ionisation Energy

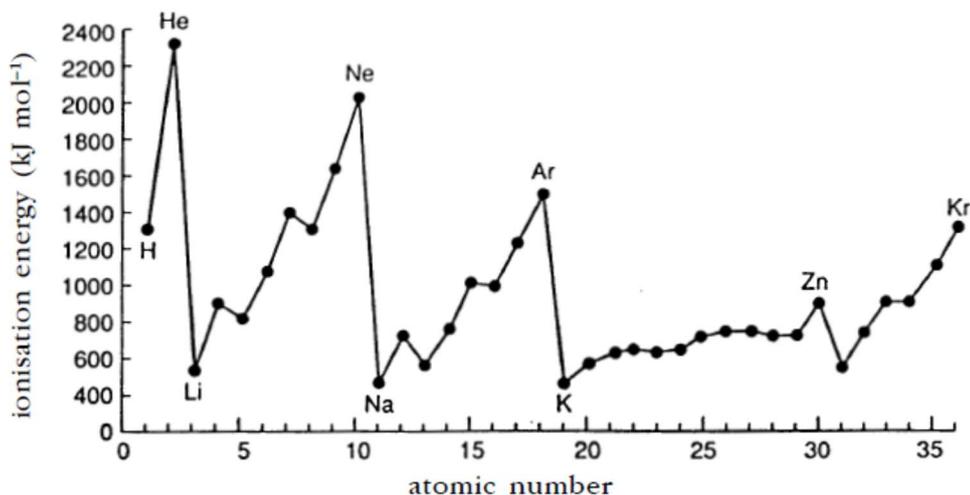
The first ionisation energy for an element E is the energy required to remove one mole of electrons from one mole of atoms in the gas state, as depicted in the equation



There are two obvious patterns. In general,

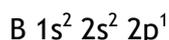
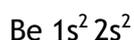
■ the ionisation energy increases across a period

■ the ionisation energy decreases down a group.



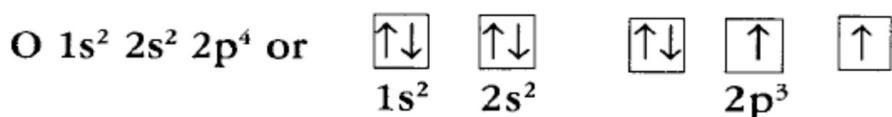
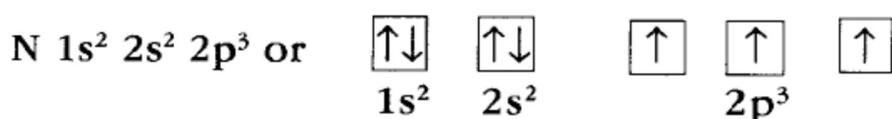
However, looking more closely, the first ionisation energies do not increase smoothly across a period. This irregularity is evidence for the existence of subshells within each shell.

For example, the reason that the first ionisation energy of boron is lower than that of beryllium can be explained by considering their electronic configurations:



Accordingly, removal of the outer electron from a boron atom involves taking one electron from the 2p subshell, but with a beryllium atom this electron comes from the full 2s subshell. Since full subshells are relatively stable, it follows that the first ionisation energy of beryllium is greater than that of boron.

A similar argument can be used to explain the higher first ionisation energy of magnesium ( $1s^2 2s^2 2p^6 3s^2$ ) compared to aluminium ( $1s^2 2s^2 2p^6 3s^2 3p^1$ ). The higher first ionisation energy of nitrogen compared to oxygen can also be explained by considering their electronic configurations:



Since half-full subshells are relatively stable and because nitrogen has a half full subshell it has a higher ionisation energy than oxygen. A similar argument can be used to explain the higher first ionisation energy of phosphorus compared to sulphur. There will also be electron-electron repulsions between two electrons in the same orbital.

Likewise, the relative values of first, second and subsequent ionisation energies can be explained in terms of the stabilities of the electronic configurations from which the electrons are removed.

For example, the sodium atom, Na, has electronic configuration  $1s^2 2s^2 2p^6 3s^1$  and the first ionisation energy of sodium is small ( $502 \text{ kJ mol}^{-1}$ ). The sodium ion,  $\text{Na}^+$ , has the electronic configuration of the noble gas neon,  $1s^2 2s^2 2p^6$ , and because this is a more stable electronic configuration, the second ionisation energy of sodium is significantly greater ( $4560 \text{ kJ mol}^{-1}$ ). This second electron to be removed from the sodium is in a shell much closer to the attraction of the nucleus and therefore much more energy is required to overcome this attraction.

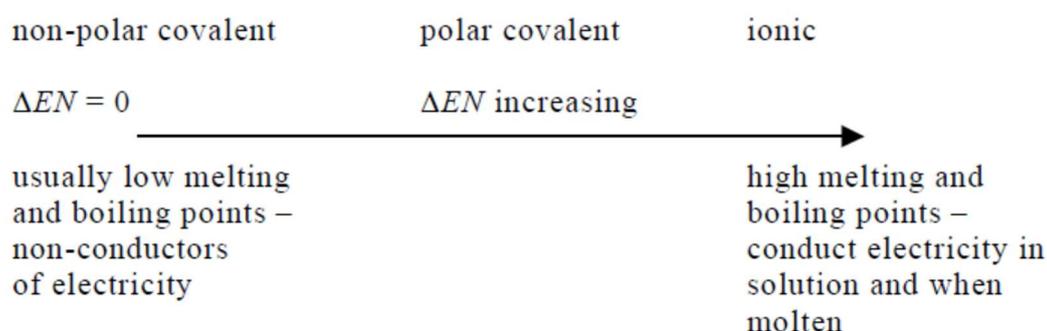
# Shapes of molecules

## Bonding and Electronegativity - Revision

A Covalent Bond will form when atoms can rearrange their electrons (by sharing) to produce an arrangement of lower energy. An Ionic Bond will form when atoms can rearrange their electrons (transfer) to produce an arrangement of lower energy.

Ionic and Covalent are, in fact, rather arbitrary labels and it is no longer enough to simply look to see if a metal element is involved or not. Ionic and Covalent are just opposite ends of a bonding continuum. Most bonds lie between these two extremes. Electronegativity values are a useful guide, but properties will still need to be studied to provide confirmation.

A simple summary of bonding covered in Higher Chemistry is shown below, where  $\Delta EN$  = difference in electronegativity values between the two atoms forming the bond.



This illustrates that non-polar covalent bonding and ionic bonding are considered as being at opposite ends of a bonding continuum with polar covalent bonding lying between these two extremes. This is very much a simplified summary with metallic bonding being ignored. There are also well-known exceptions such as carbon in the form of graphite, which can conduct electricity.

Electronegativity differences between atoms of different elements are helpful but do not always predict the type of bonding correctly. For example, consider the two compounds sodium hydride (NaH) and water (H<sub>2</sub>O):

sodium hydride: EN for Na = 0.9 EN for H = 2.2

so  $\Delta EN = 2.2 - 0.9 = 1.3$

water: EN for H = 2.2 EN for O = 3.5

so  $\Delta EN = 3.5 - 2.2 = 1.3$

It might therefore be expected that both compounds will have the same type of bonding, most likely polar covalent.

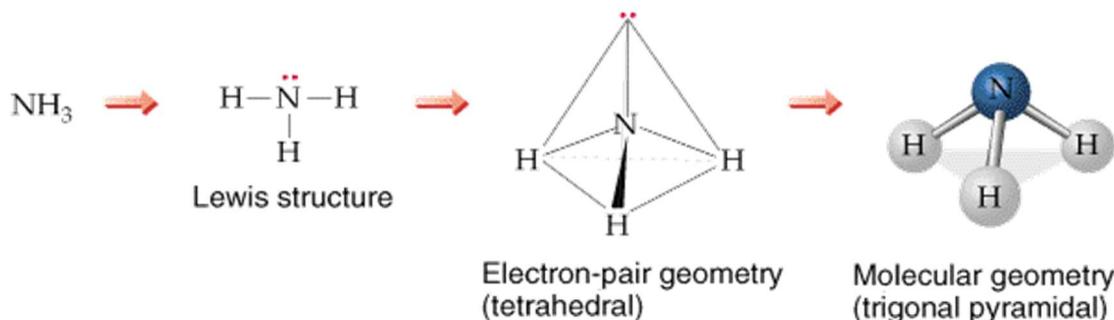
However, sodium hydride is a solid at room temperature and when melted and electrolysed, hydrogen gas is produced at the positive electrode. This demonstrates that sodium hydride is ionic and also that it contains the hydride ion, H<sup>-</sup>. Water, of course, has polar covalent bonding.

Electronegativity values and their differences are useful indicators of the type of bonding but it is also necessary to study the properties of the substance for confirmation or otherwise.

## VSEPR Rules

In order to predict molecular shape, we consider that all outer shell electrons (valence electrons) of the central atom repel each other. Therefore, the molecule adopts whichever 3D geometry minimizes this repulsion. Both bonding and non-bonding electron pairs must be considered.

We call this process the Valence Shell Electron Pair Repulsion (VSEPR) theory.



The shapes of molecules or polyatomic ions (e.g. NH<sub>4</sub><sup>+</sup>) can be predicted from the number of bonding electron pairs and the number of non-bonding electron pairs (lone pairs). This is because the direction which covalent bonds take up in space is determined by the number of orbitals occupied by electron pairs and the repulsion between these orbitals. The repulsive effect of a nonbonded pair or lone pair of electrons is greater than that of a bonded pair and so the trend in repulsive effect is:

bonded pair:bonded pair < bonded pair:lone pair < lone pair:lone pair

The shape adopted by the molecule or polyatomic ion is the one in which the electron pairs in the outer shell get as far apart as possible. In other words, the shape in which there is the minimum repulsion between the electron pairs.

It is important not to confuse the number of atoms with the number of electron pairs.

For example, CF<sub>4</sub> and XeF<sub>4</sub> may, at first sight, appear likely to be the same shape.

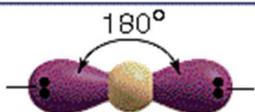
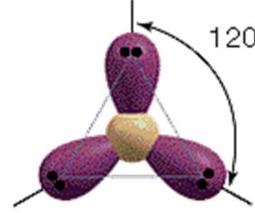
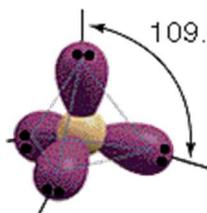
$$\text{Electron pairs} = \frac{\text{electrons of central atom} + \text{no. of atoms attached}}{2}$$

$$\text{CF}_4 = \frac{4+4}{2} = 4 \text{ pairs.}$$

$$\text{XeF}_4 = \frac{10+4}{2} = 6 \text{ pairs.}$$

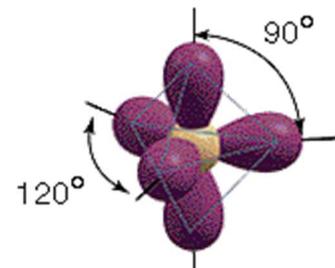
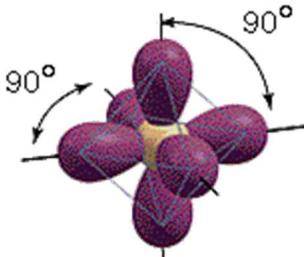
To minimise repulsion, the electron pairs arrange themselves in given shapes:

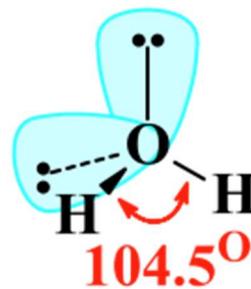
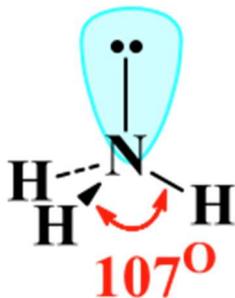
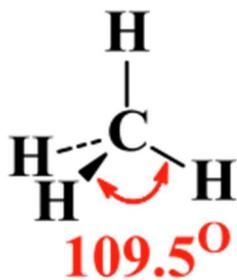
**ELECTRON-PAIR GEOMETRIES AS A FUNCTION OF THE NUMBER OF ELECTRON PAIRS**

Number of Electron Pairs	Arrangement of Electron Pairs	Electron-Pair Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°

Bonding electrons, because they are attracted by two nuclei, do not repel as much as non-bonding electrons. This can cause 'distortions' in the shapes of molecules:

**ELECTRON-PAIR GEOMETRIES AS A FUNCTION OF THE NUMBER OF ELECTRON PAIRS**

Number of Electron Pairs	Arrangement of Electron Pairs	Electron-Pair Geometry	Predicted Bond Angles
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90° 180°



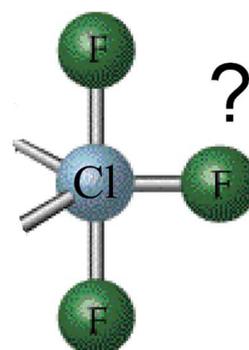
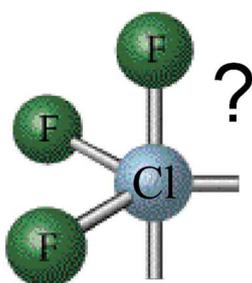
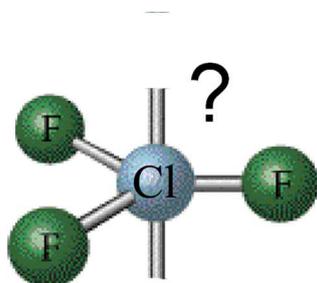
Since lone pairs repel more than bonding pairs, this leads to a wide range of shapes within different molecules:

Electron pair repulsions decrease in strength in the order:

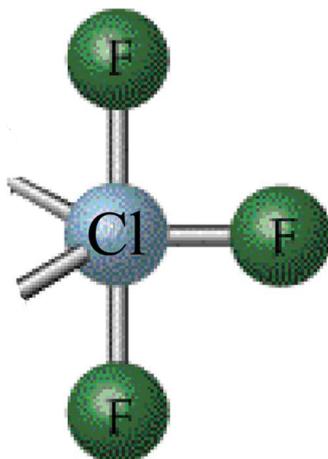
non-bonding/non-bonding

non-bonding/bonding

bonding/bonding

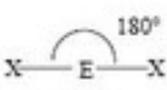
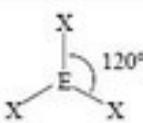
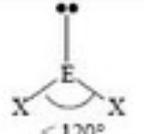
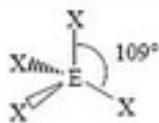
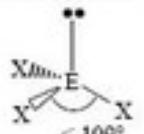
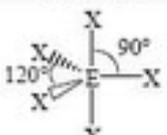
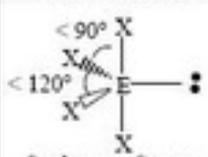
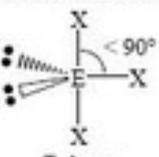
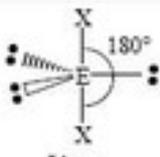
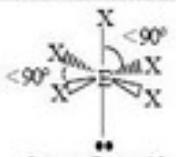
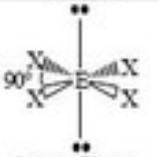
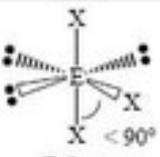
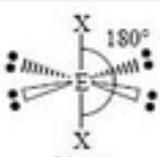


Placing the non-bonding lone pairs at the Axial positions would appear to give least repulsion but they would only be 90° away from the 3 bonding pairs. To minimize e<sup>-</sup> - e<sup>-</sup> repulsion, lone pairs are always placed in equatorial positions, so ...



The final shape of the bonds in the molecule are T-shaped, although the electron pairs take up an octahedral shape.

Total number of electron pairs	Arrangement of electron pairs
2	Linear
3	Trigonal
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

VSEPR Geometries					
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 <p>Linear</p>				
3	 <p>Trigonal Planar</p>	 <p>Bent or Angular</p>			
4	 <p>Tetrahedral</p>	 <p>Trigonal Pyramid</p>	 <p>Bent or Angular</p>		
5	 <p>Trigonal Bipyramid</p>	 <p>Sawhorse or Seesaw</p>	 <p>T-shape</p>	 <p>Linear</p>	
6	 <p>Octahedral</p>	 <p>Square Pyramid</p>	 <p>Square Planar</p>	 <p>T-shape</p>	 <p>Linear</p>

## (c) Transition Metals

### (i) Transition Metal Compounds

The transition metals are found in the d-block of the periodic table and strictly speaking are the metals in which the d-subshell is incomplete or being filled. This means that Cu and Zn are not strictly transition metals, although we commonly group them as transition metals (see table below).

Element	Electronic configuration	
	Spectroscopic notation	Orbital box notation (d electrons only)
Scandium	[Ar] 3d <sup>1</sup> 4s <sup>2</sup>	↑ □ □ □ □
Titanium	[Ar] 3d <sup>2</sup> 4s <sup>2</sup>	↑ ↑ □ □ □
Vanadium	[Ar] 3d <sup>3</sup> 4s <sup>2</sup>	↑ ↑ ↑ □ □
Chromium	[Ar] 3d <sup>5</sup> 4s <sup>1</sup>	↑ ↑ ↑ ↑ ↑
Manganese	[Ar] 3d <sup>5</sup> 4s <sup>2</sup>	↑ ↑ ↑ ↑ ↑
Iron	[Ar] 3d <sup>6</sup> 4s <sup>2</sup>	↑↓ ↑ ↑ ↑ ↑
Cobalt	[Ar] 3d <sup>7</sup> 4s <sup>2</sup>	↑↓ ↑↓ ↑ ↑ ↑
Nickel	[Ar] 3d <sup>8</sup> 4s <sup>2</sup>	↑↓ ↑↓ ↑↓ ↑ ↑
Copper	[Ar] 3d <sup>10</sup> 4s <sup>1</sup>	↑↓ ↑↓ ↑↓ ↑↓ ↑↓
Zinc	[Ar] 3d <sup>10</sup> 4s <sup>2</sup>	↑↓ ↑↓ ↑↓ ↑↓ ↑↓

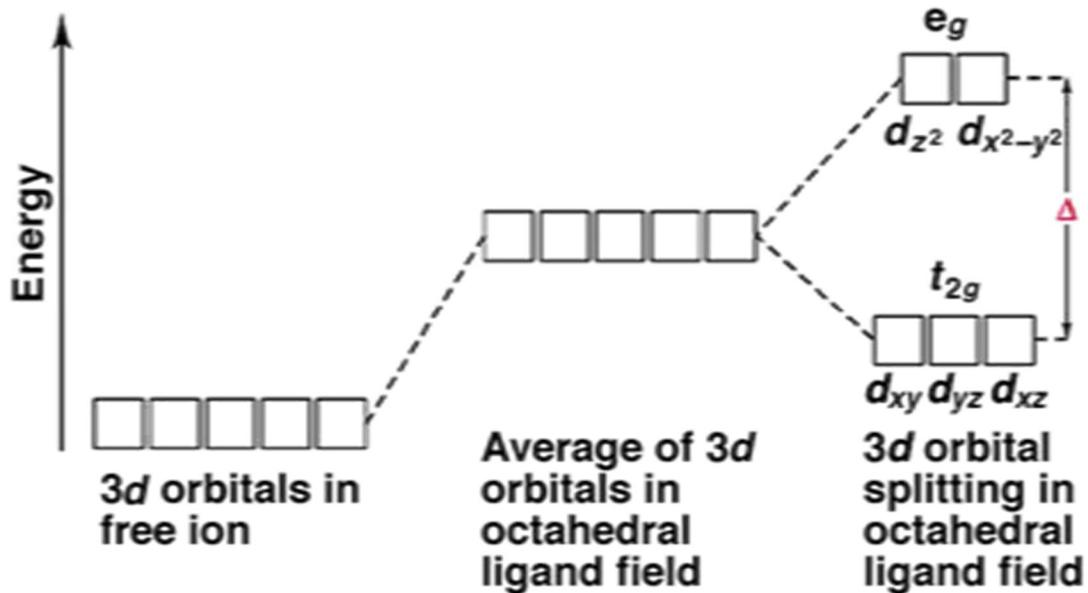
Note that Cr and Cu follow different rules in terms of their filling of 4s before 3d. This is because the filled (or exactly half filled) orbitals confer an energetic stability.

#### Colour in Transition Metal Compounds

Simple ions and complex ions of the transition metals are often coloured. This is because they **absorb** light in certain parts of the visible spectrum. The colour seen is the complementary colour to that absorbed, i.e. it is a combination of the colours not absorbed. To understand this outcome, it has to be appreciated that white light is a combination of the three primary colours red, blue and green.

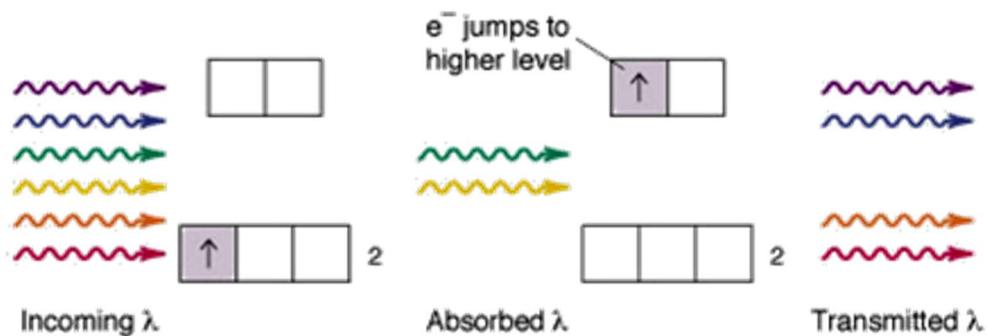
If red light is absorbed, the colours transmitted are blue and green, which is seen as green/blue or cyan. If blue light is absorbed, the colours transmitted are red and green, which is seen as yellow.

When transition metals with an incomplete d subshell bond to other species (or **ligands**), the energies of the d-orbitals are changed so that they are no longer degenerate (i.e. that are not all the same energy any more).



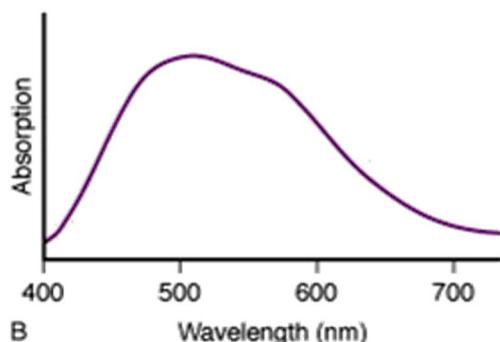
Different species (ligands) bonded to the central transition metal ion produce different splits in the d-orbitals, and it is the size of this split which determines the colour produced by the compound or complex.

e.g. in  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

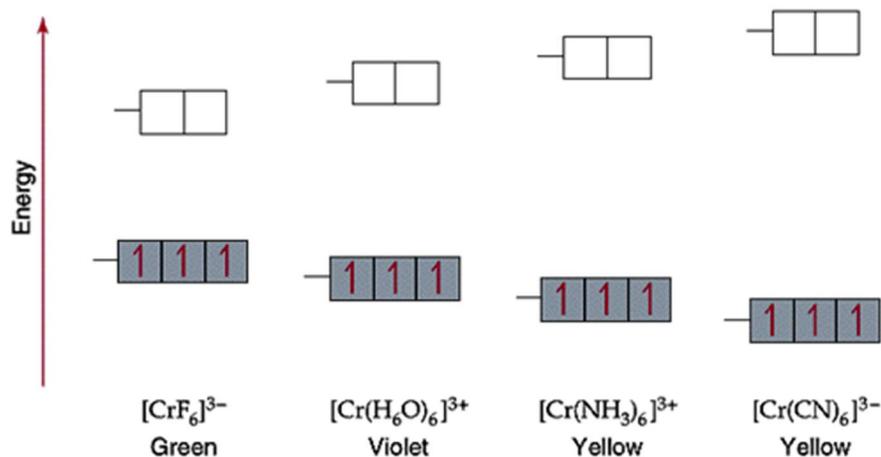
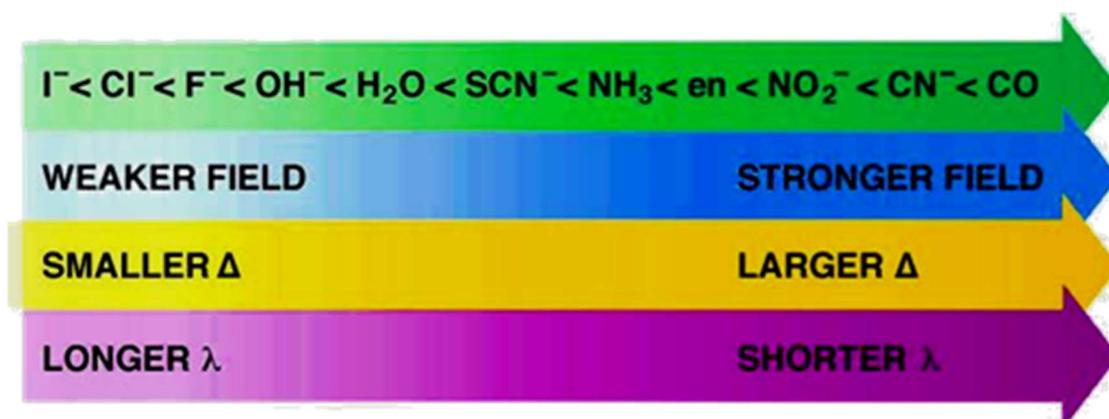


Green-yellow light is absorbed as an electron is promoted from one set of d-orbitals to the other set of d-orbitals.

**d → d transitions.** The blue & red light transmitted makes the compound a purple colour



Ligands can be ordered according to the size of the d orbital split they produce when bonded to a transition metal:



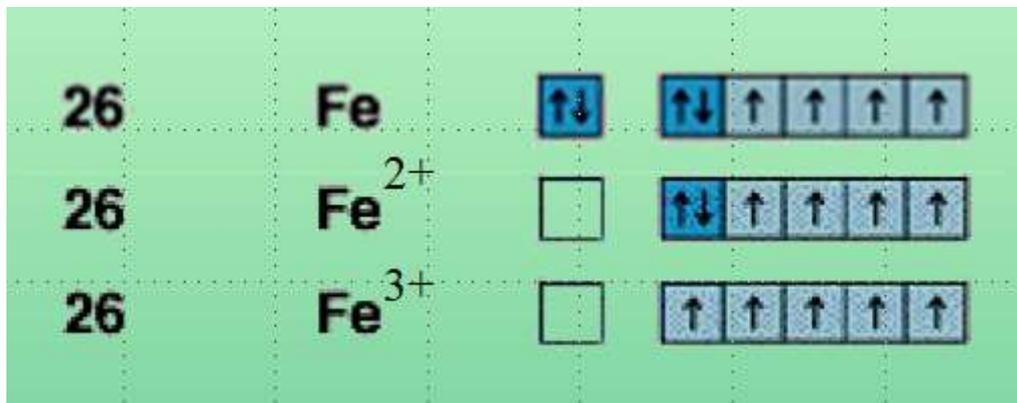
NB: colour will only be produced if there is space for a d electron to make a transition between the lower level and the higher level orbitals.

### Oxidation Number in Transition Metal Compounds

**Oxidation numbers** are a way of keeping track of electrons. The oxidation state of an atom or ion represents the number of electrons lost or gained relative to the ground state (stable) atom. They do not necessarily represent the 'true' charge on a particle but they work!

Transition metals exhibit **variable oxidation states of differing stability**. Transition metals exhibit **variable oxidation states** because they can not only lose their 4s electrons but some or all of their 3d electrons.

Sometimes **electron configurations** can be used to explain why one **oxidation state** is more stable. For example, during rusting  $\text{Fe}^{2+}$  ions are formed first, but they then change into  $\text{Fe}^{3+}$  ions.



The  $\text{Fe}^{3+}$  ion forms in preference to  $\text{Fe}^{2+}$  because of the **extra stability** associated with **all the d-orbitals being half-filled**.

#### Rules for Working Out Oxidation Number

- Rule 1** Simple ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  etc continue to count as + 1 or - 1 .
- Rule 2** Oxygen is always assumed to be - 2 .
- Rule 3** Hydrogen is always assumed to be +1
- Rule 4** Overall charge on a compound is always 0 .
- Rule 5** In polyatomic ions, the sum of all the oxidation numbers is equal to the overall charge on the ion.

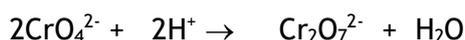
**What is the oxidation number for Cr in  $\text{CrO}_4^{2-}$  ?**

- Rule 2.** We assume each oxygen is -2, so  $4 \times 0 = - 8$
- Rule 5.** Overall charge on ion is -2, so Cr must be +6 .

**What is the oxidation number for Cr in  $\text{Cr}_2\text{O}_7^{2-}$  ?**

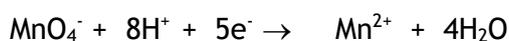
- Rule 2.** We assume each oxygen is -2, so  $7 \times 0 = - 14$
- Rule 5.** Overall charge on ion is -2, so  $2 \times \text{Cr}$  must be +12  
so Cr must be +6

When chromate ions react to form dichromate ions we can calculate that no electrons are gained or lost.



**Compounds containing metals in a high oxidation state tend to be oxidising agents**

e.g.



**Compounds containing metals in a low oxidation state tend to be reducing agents**

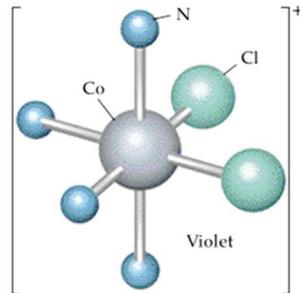
e.g.



Oxidation results in an increase in the oxidation number whereas reduction results in a decrease in the oxidation number.

### Transition Metal Complexes and Names

A transition metal complex is a **Metal** (atom or ion), **surrounded by ligands**, with the ligands bound to the metal through **coordinate covalent bonds**. The ligand is an atom, molecule or ion that contains at least one **lone pair**.



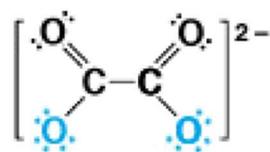
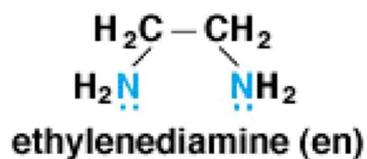
Monodentate ligands: Can only form **one bond** with the metal atom/ion:

$\text{NH}_3$  = ammine

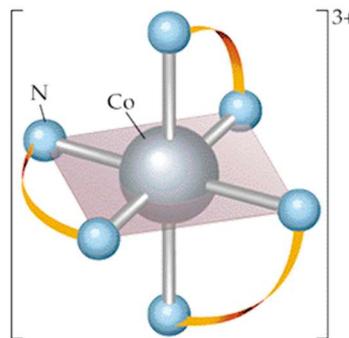
$\text{OH}_2$  = aqua

$\text{Cl}^-$  = chlorido

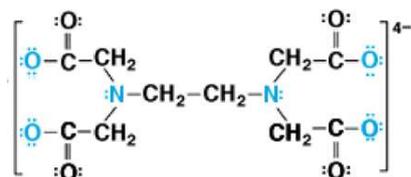
Bidentate ligands: Can form **two bonds** with the metal atom/ion



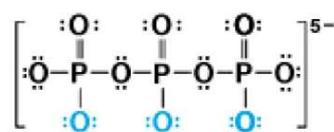
oxalate ion



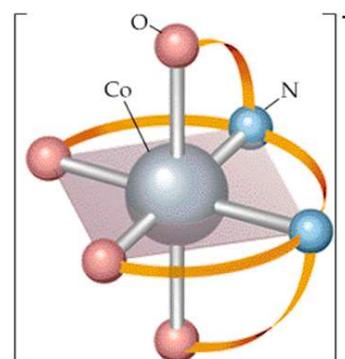
Polydentate ligands: Can form **many bonds** with the metal atom/ion:



ethylenediaminetetraacetate (EDTA) ion



triphosphate ion



## Naming Complexes

To name a complex salt (containing positive and negative ion), use the normal chemistry rules i.e. name the positive ion first, then the negative ion. To do this, we need to know the rules for naming the complex ion:

## Naming complex ions

Complex ions and complexes are written and named according to IUPAC rules. The formula of a complex ion should be enclosed within square brackets, although common complexes such as  $\text{MnO}_4^-$  are often written without brackets. The metal symbol is written first, then the negative ligands followed by the neutral ligands, e.g.  $[\text{Fe}(\text{OH})_2(\text{OH}_2)_4]^+$ .

1. The name of the complex part has two parts written as one word. The ligands are named first and the central metal ion second.
2. Give the ligand name and the number of each (di-, tri-, etc). (see a below)
3. Give the metal name followed by the oxidation number in brackets. The overall charge on the complex part will equal the oxidation number plus the total charge on the ligands.
4. If the complex ion is negative, the metal name is followed by the suffix-ate and then the oxidation number in brackets. (see b below)

When naming the complex ion or molecule the ligands should be named first, in alphabetical order (not including any numerical prefix), followed by the name of the metal. If the ligand is a negative ion the name of which ends in -ide, the ending changes to 'o', e.g. chloride,  $\text{Cl}^-$ , becomes chlorido, cyanide,  $\text{CN}^-$ , becomes cyanido, nitrite,  $\text{NO}_2^-$ , changes to nitrito.

Conventional name	Formula	Name in Complex
Ammonia	$\text{NH}_3$	ammine
Carbon Monoxide	$\text{CO}$	carbonyl
Chloride	$\text{Cl}^-$	chlorido
Cyanide	$\text{CN}^-$	cyanido
Oxalate	$\text{C}_2\text{O}_4^{2-}$	oxalato
Oxide	$\text{O}^{2-}$	oxido
Water	$\text{OH}_2$	aqua

Changing metal names to 'ate' in negative ions:

Vanadium	Vanadate
Chromium	Chromate
Manganese	Manganate
Copper	Cuprate
Cobalt	Cobaltate
Iron	Ferrate
Nickel	Nickelate
Tin	Stannate
Lead	Plumbate

Example: Naming  $\text{Na}_3[\text{Co}(\text{F})_6]$

The positive ion name precedes the negative ion name. So the correct name will be sodium.....then the complex ion.

Name the ligand then the metal in the complex ion.

Six fluoride ligands gives 'hexafluorido-'.

The next step is find out the oxidation number of cobalt in  $\text{Na}_3[\text{Co}(\text{F})_6]$

a) Since there are three sodium ions, the overall charge on the complex ion must be 3-

b) There are six fluoride ions surrounding a central cobalt ion, each with a charge of 1-

So, (oxidation number of Co) + 6 (-1) = -3

So, oxidation number of Co = -3 + 6 = +3

Cobalt is the central metal ion., with an oxidation number of 3.

Since the complex ion is a negative ion (anion), this gives 'cobaltate(III)'.

The positive ion name precedes the negative ion name. So the correct name becomes **Sodium hexafluoridocobaltate(III)**

**Questions:**

Name the following complexes:

- (a)  $[\text{CoCl}_4]^{2-}$
- (b)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
- (c)  $[\text{Fe}(\text{CN})_6]^{4-}$
- (d)  $[\text{Ti}(\text{NH}_3)_6]^{3+}$
- (e)  $[\text{Ni}(\text{CN})_6]^{4-}$
- (f)  $\text{MnO}_4$
- (g)  $[\text{PtCl}_6]^{2-}$

# Glossary

Word	Meaning
aufbau principle	This states that orbitals are filled in order of increasing energy.
bidentate	A ligand that contains two atoms with lone pairs of electrons capable of bonding to a metal ion.
complex	A complex consists of a central metal ion surrounded by ligands.
coordination compounds	Compounds in which a central metal ion is attached to a group of surrounding molecules or ions by dative covalent bonds (also known as coordinate bonds).
coordination number	The coordination number is the number of nearest neighbours by which an atom or ion is surrounded in a structure.
dative covalent bond	In this type of covalent bond, both the shared electrons originally came from the same atom
degenerate	A set of atomic orbitals that are of equal energy to each other are said to be degenerate.
electromagnetic spectrum	This is the range of frequencies or wavelengths of electromagnetic radiation.
electronegativity	Electronegativity is a measure of the attraction an atom involved in a bond has for the electrons of the bond.
Frequency	This is the number of wavelengths that pass a fixed point in one unit of time.
ground state	This is the lowest possible electronic configuration the electrons in an atom can adopt.
Heisenberg's uncertainty principle	This states that it is impossible to state precisely the position and the momentum of an electron at the same instant.
hexadentate	A ligand that bonds to a metal ion using electron pairs on six donor atoms.
Hund's rule	When degenerate orbitals are available, electrons fill each singly, keeping their spins parallel before pairing starts.
hybridisation	the mathematical combination of atomic orbitals to generate new orbitals that will more effectively form bonds.
Ligands	Molecules or ions that bond to the central metal ion in a complex.
molecular orbital	A molecular orbital is a region in space between the nuclei where there is a high probability of finding electrons. It is formed by the overlap of atomic orbitals.

monodentate	A ligand that bonds to a metal ion using the electron pair of a single donor atom.
oxidation	This is the loss of electrons from a substance. It can also be described as an increase in oxidation number.
oxidation number	The formal charge assigned to each atom in a compound according to certain rules.
Pauli exclusion principle	This states that an orbital holds a maximum of two electrons.
reduction	This is the gain of electrons by a substance. It can also be described as a decrease in oxidation number.
spectrochemical series	A list of ligands in order of the size of the crystal field splitting caused in the d orbitals.
Wavelength	This is the distance between adjacent crests or troughs of a wave.
wavenumber	Wavenumber is the reciprocal of wavelength and has the units of $\text{cm}^{-1}$ (number of cycles per cm.)