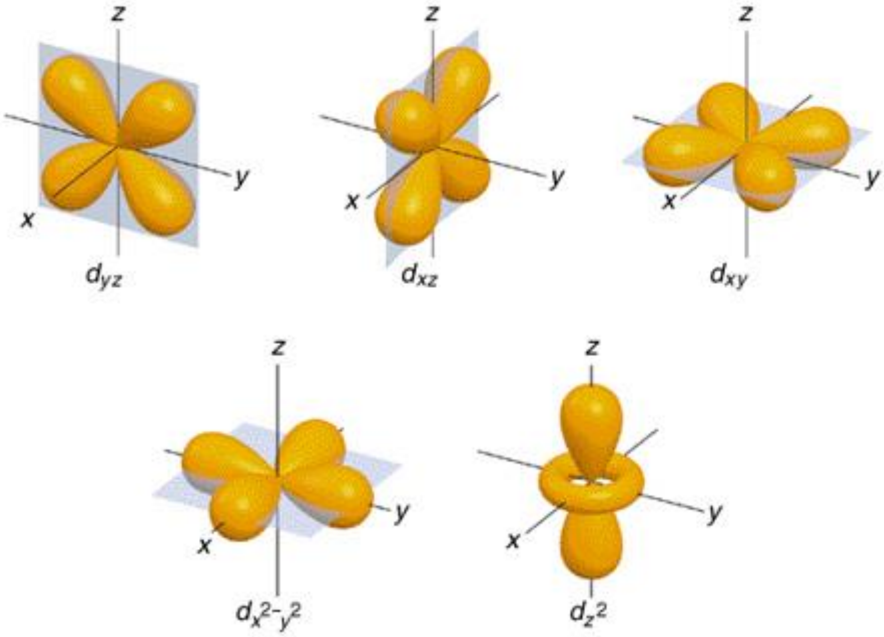
Cathkin High School
CfE Advanced Higher Chemistry

Unit 1
Inorganic and Physical Chemistry



Pupil Notes

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?	☺ 😐 ☹

No.	Learning Outcome	Understanding?
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?	☺ 😐 ☹
19	What does it mean if a reaction is in dynamic equilibrium?	☺ 😐 ☹
20	How can the equilibrium constant, K, be used to predict the position of equilibrium and/or calculate the concentration of species at equilibrium?	☺ 😐 ☹
21	What is the mathematical relationship between pH and the concentration of H^+ ions in solution?	☺ 😐 ☹
22	How can the ionic product of water, $Kw=[OH^-][H^+]$, be used to calculate the concentrations of the two ions in aqueous solutions?	☺ 😐 ☹
23	How do Bronsted and Lowry define an acid and a base?	☺ 😐 ☹
24	What is a 'conjugate' acid or base?	☺ 😐 ☹
25	What is a 'strong' acid or base as opposed to a 'weak' acid or base?	☺ 😐 ☹
26	Are all salts neutral? How can the pH of a salt be predicted?	☺ 😐 ☹
27	How does the equilibrium constant for a weak acid or base relate to its strength?	☺ 😐 ☹
28	What is the pKa value for an acid?	☺ 😐 ☹
29	How can the pH of a weak acid be calculated?	☺ 😐 ☹
30	How do buffer solutions work and how are they made?	☺ 😐 ☹

No.	Learning Outcome	Understanding?
31	How can the pH of a buffer solution be calculated?	☺ 😐 ☹
32	What is equation for the equilibrium of a weak acid indicator?	☺ 😐 ☹
33	How do you predict the pH at which an indicator will change colour?	☺ 😐 ☹
34	What is the standard enthalpy of formation?	☺ 😐 ☹
35	What is the mathematical definition for enthalpy of formation for an element?	☺ 😐 ☹
36	What is entropy and how does it change with the physical state of substances?	☺ 😐 ☹
37	What is the Second Law of Thermodynamics?	☺ 😐 ☹
38	What is the Third Law of Thermodynamics?	☺ 😐 ☹
39	How can the change in entropy of a reaction system be calculated?	☺ 😐 ☹
40	What is the relationship between standard entropy, standard enthalpy and free energy (ΔG^o)	☺ 😐 ☹
41	How can ΔG^o be used to predict whether a reaction will occur or not?	☺ 😐 ☹
42	What does the term 'order of reaction' mean?	☺ 😐 ☹
43	How can a rate equation be derived from the experimental data for a reaction?	☺ 😐 ☹
44	How can the rate constant, k, be determined from initial rate data?	☺ 😐 ☹
45	What is the 'rate determining step' in a reaction?	☺ 😐 ☹
46	How can the rate equation be used to predict which reactants take part in the rate determining step?	☺ 😐 ☹

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 3×10^8 m $s^{-1.}$

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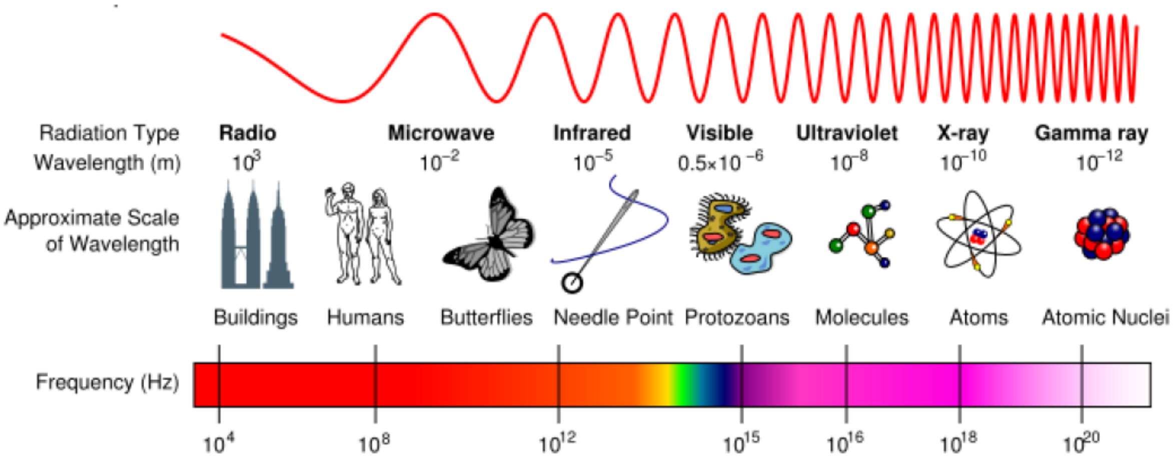


➤ ➤ ➤ Energy Increases and Frequency Increases ➤ ➤ ➤

◀ ◀ ◀ 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 λ (lambda).

All waves have a characteristic ***wavelength*** λ, measured in metres **(m)** to nanometres **(nm)**

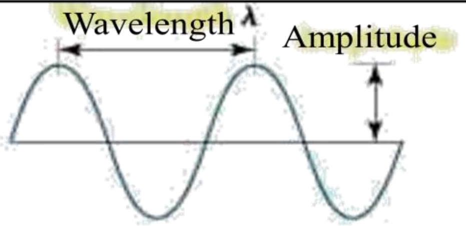
The ***frequency***, f, of a wave is the number of waves which pass a point in one second measured in **Hertz (Hz)** or per seconds **(s^{-1})**

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

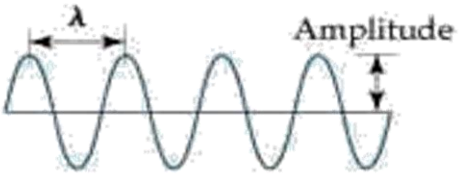
$$c = f\lambda$$

For light, $c = 3.00 \times 10^8\ ms^{-1}$

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



(a) Two complete cycles of wavelength λ



(b) Wavelength half of that in (a); frequency twice as great as in (a)

(c) Same frequency as (b), smaller amplitude

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*** (6.63×10^{-34} 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:

$$E = Lhf \qquad \textbf{or} \qquad E = L\,h\,c\,/\,\lambda$$

Where L is the ***Avogadro Constant***, 6 .02 x 10^{23} and E would now be in J mol^{-1} or kJ mol^{-1}.

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

640 nm = 640×10^{-9} m = 6.40×10^{-7} m.

For each ***photon***:

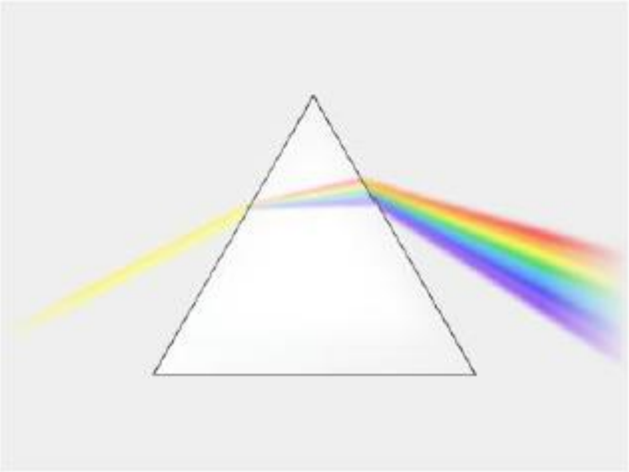
$$\begin{aligned} E &= h\,c\,/\,\lambda \\ &= (6.63 \times 10^{-34} \times 3.00 \times 10^{8}) / 6.40 \times 10^{-7} \\ &= 3.11 \times 10^{-19}\ \text{J} \end{aligned}$$

For ***1 mole of photons***:

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

Atomic Spectra

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



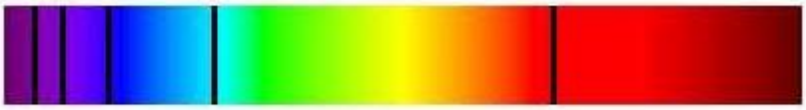
Emission Spectra

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.

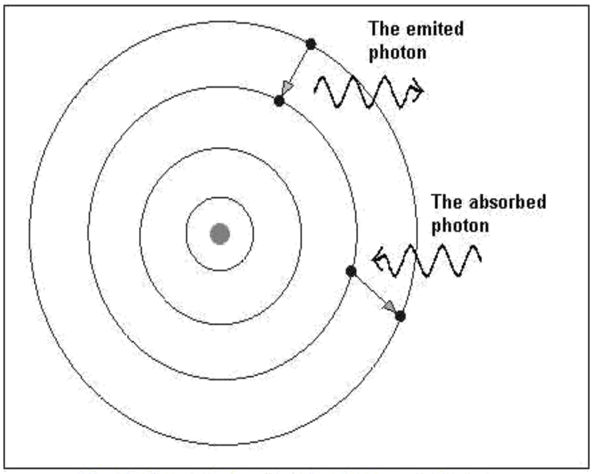
Absorption Spectra

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.***



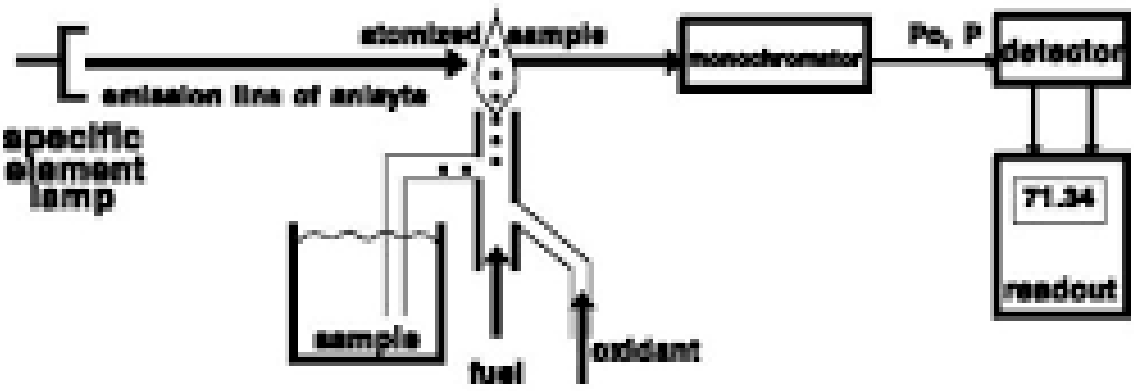
The electron emits or absorbs the energy changing the orbits.

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.

Atomic Spectroscopy with Flames

Atomic Absorption Spectroscopy



Po = light intensity w/ blank

P = light intensity w/ sample

A = log[Po/P] = kbC

b = flame path; C = sample concn

k depends on absorptivity and flow

$A \; \alpha \; C$

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:

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

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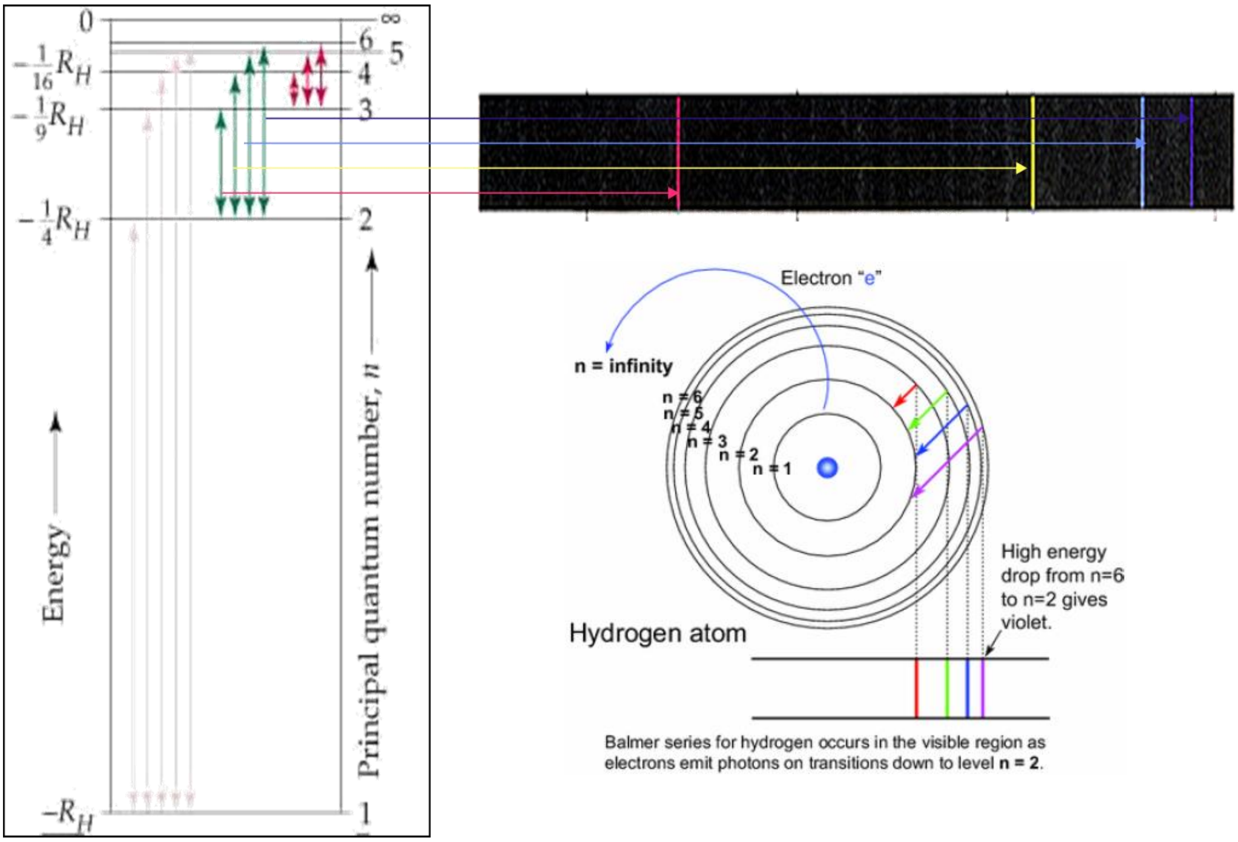
After lots of maths, Bohr showed that

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

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



Balmer series for hydrogen occurs in the visible region as electrons emit photons on transitions down to level **n = 2**.

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

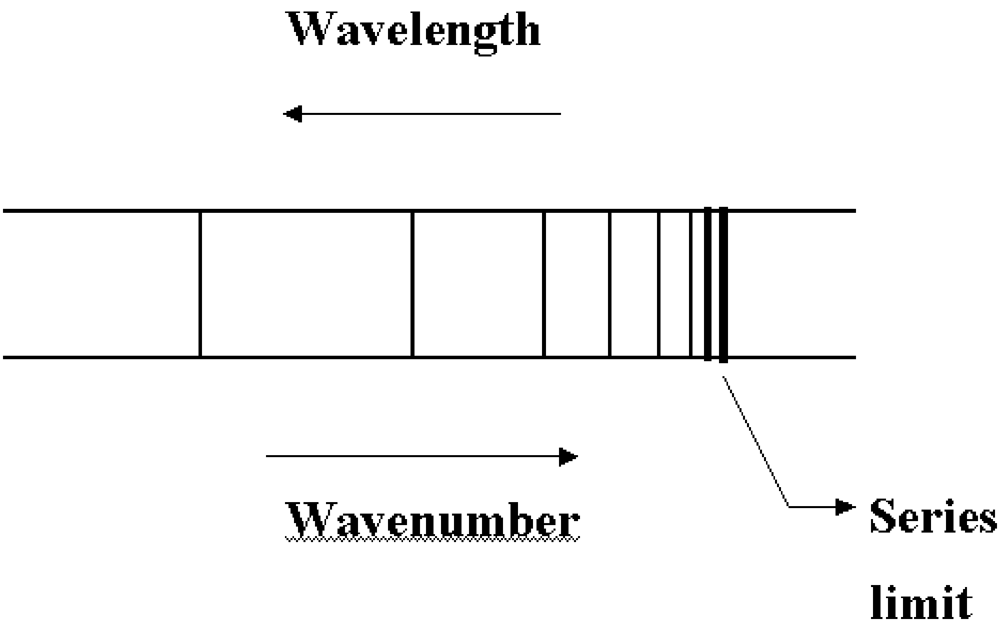
Another series of lines called the ***Lyman Series*** are due to electrons returning to the ***n=1*** level. The ΔE values are higher and the lines appear in the ***ultra-violet*** region.

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 nm = 91.2×10^{-9} m = 9.12×10^{-8} m.

For each ***photon***:
$E = hc/\lambda$
$= 6.63 \times 10^{-34} \times 3.00 \times 10^{8} / 9.12 \times 10^{-8}$
$= 2.18 \times 10^{-18}$ J

For ***1 mole of photons***:
$E = 2.18 \times 10^{-18} \times 6.02 \times 10^{23}$ J
$= 1.31 \times 10^{6}$ J mol^{-1}
$= 1{,}310$ k J mol^{-1}

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	1*s*
2	0	2*s*
	1	2*p*
3	0	3*s*
	1	3*p*
	2	3*d*

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

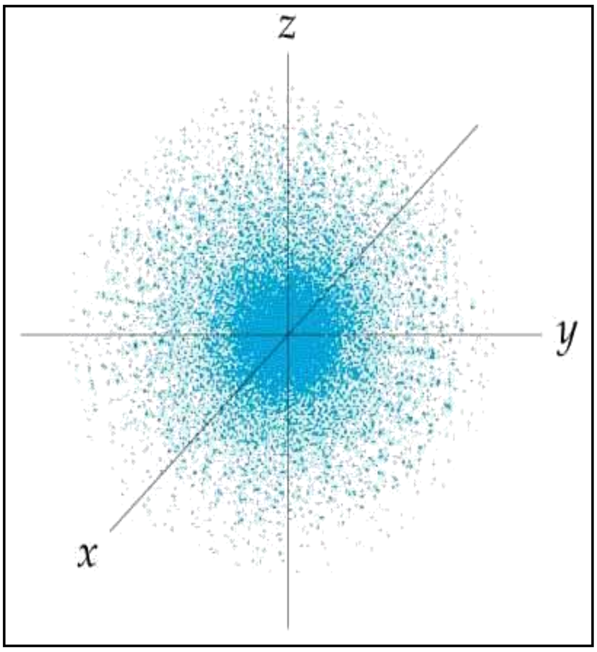
Sub-shell name	Possible value: ℓ	Possible value: *m*
1*s*	0	0
2*s*	0	0
2*p*	1	-1, 0,+1
3*s*	0	0
3*p*	1	-1, 0,+1
3*d*	2	-2,-1, 0,+1,+2

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

s-orbital

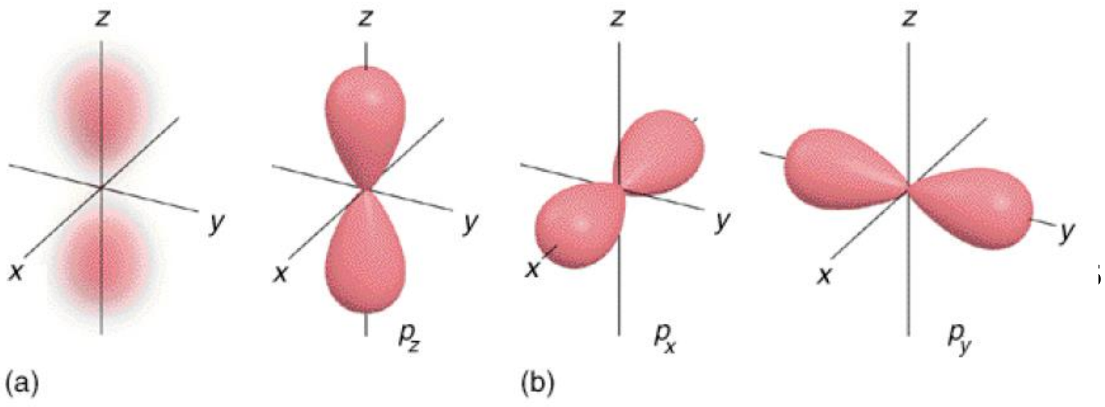
Quantum mechanics has shown that ***s orbitals*** are ***spherical*** in shape

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



p-orbitals

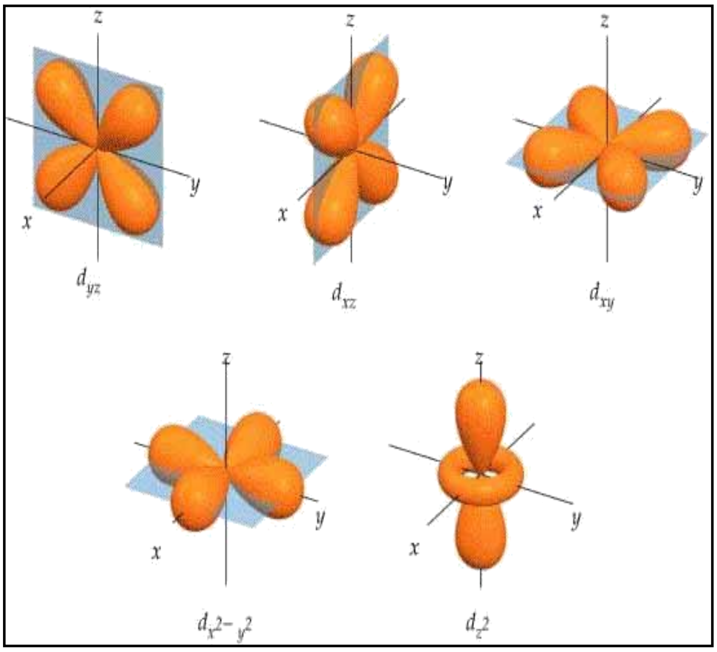
The ***shape*** of a ***p-orbital*** is ***dumb-bell***, ($l = 1$).
Each shell, from the second shell onwards, contains ***three*** of these ***p-orbitals***, ($m_l = -1 \quad 0 \quad +1$).



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

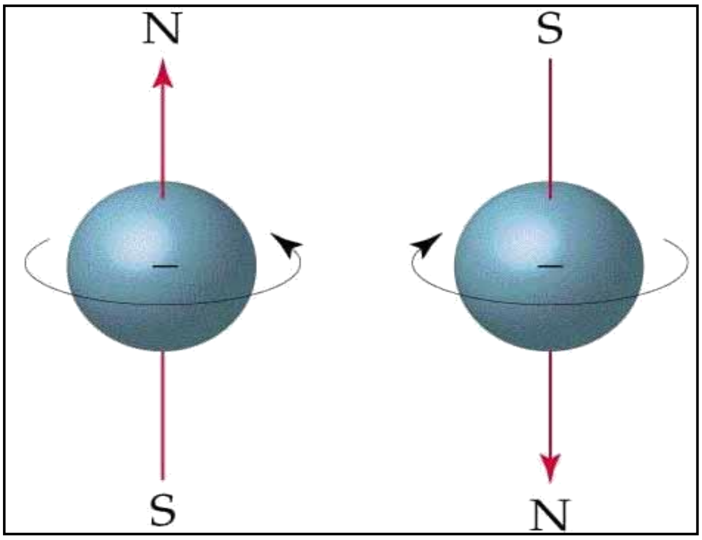
d-orbitals

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'*, $d_x2\ -_y2$ and *'along the z-axis'*, d_z2

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.

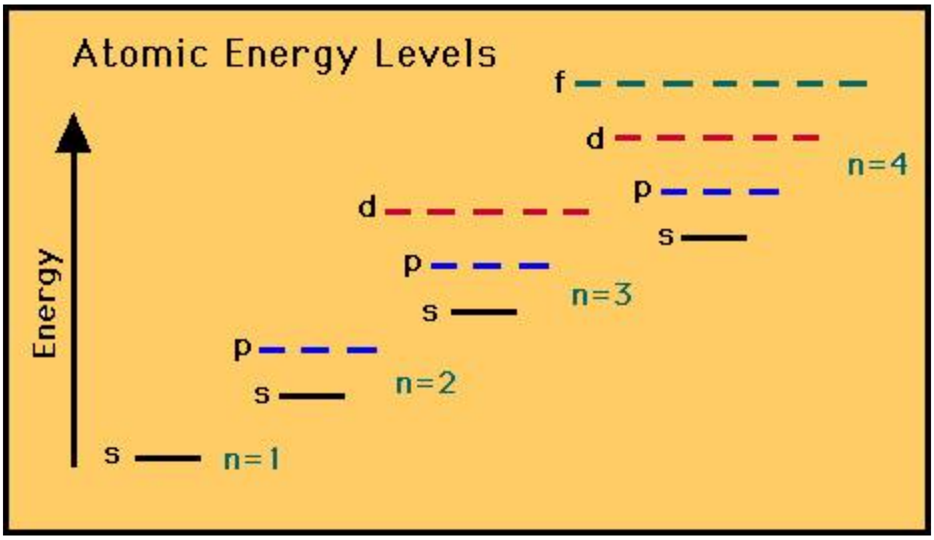
Electron Configuration

There are 3 rules which determine in which orbitals the electrons of an element are located.

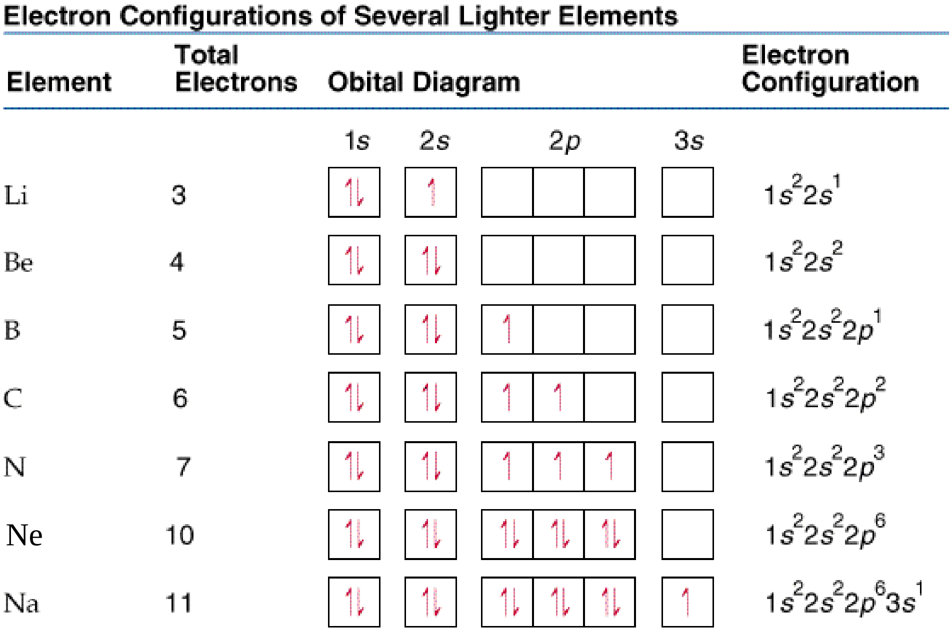
1. The ***Aufbau Principle*** states that ***electrons will fill orbitals starting with the orbital of lowest energy***.
2. For ***degenerate*** orbitals, ***electrons fill each orbital singly before any orbital gets a second electron*** (***Hund's Rule of Maximum Multiplicity***).
3. The ***Pauli Exclusion 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).
4.

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:



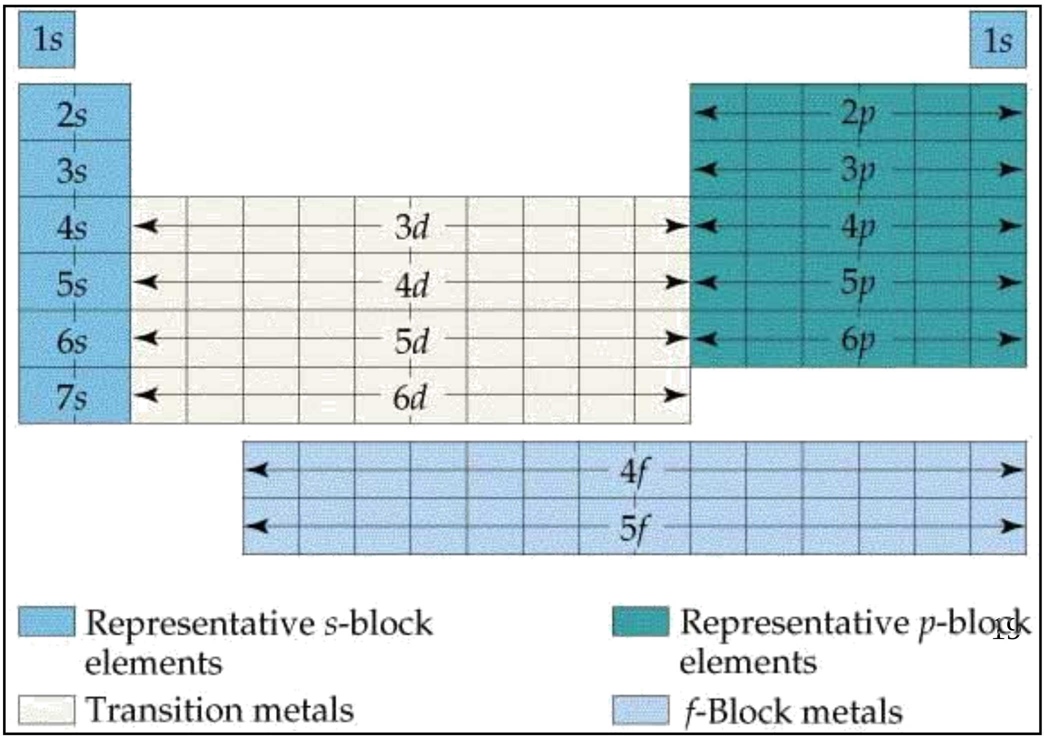
Electron Configurations of Several Lighter Elements

Element	Total Electrons	Obital Diagram					Electron Configuration
		1s	2s	2p			3s	
Li	3	↑↓	↑					$1s^22s^1$
Be	4	↑↓	↑↓					$1s^22s^2$
B	5	↑↓	↑↓	↑				$1s^22s^22p^1$
C	6	↑↓	↑↓	↑	↑			$1s^22s^22p^2$
N	7	↑↓	↑↓	↑	↑	↑		$1s^22s^22p^3$
Ne	10	↑↓	↑↓	↑↓	↑↓	↑↓		$1s^22s^22p^6$
Na	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑	$1s^22s^22p^63s^1$

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

The PeriodicTable

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

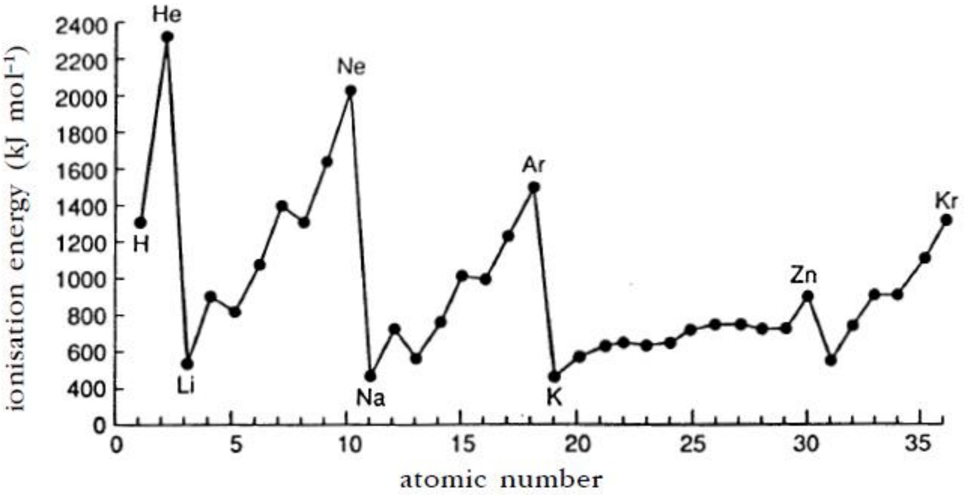


Ionisation Energy

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

$$E(g) \rightarrow E^+(g) + e^-$$

There are two obvious patterns. In general,
- the ionisation energy increases across a period
- the ionisation energy decreases down a group.



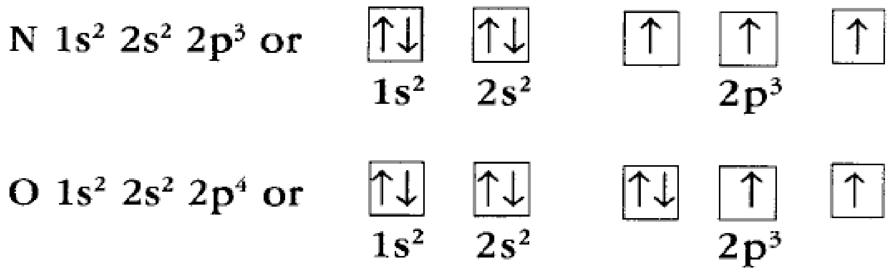
However, looking more closely, it can be seen that the first ionisation energies do not increase smoothly across a period. This irregularity is evidence for the existence of subshells within each shell.

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:

Be $1s^2\ 2s^2$
B $1s^2\ 2s^2\ 2p^1$

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 kJ mol^{-1}). The sodium ion, 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 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.

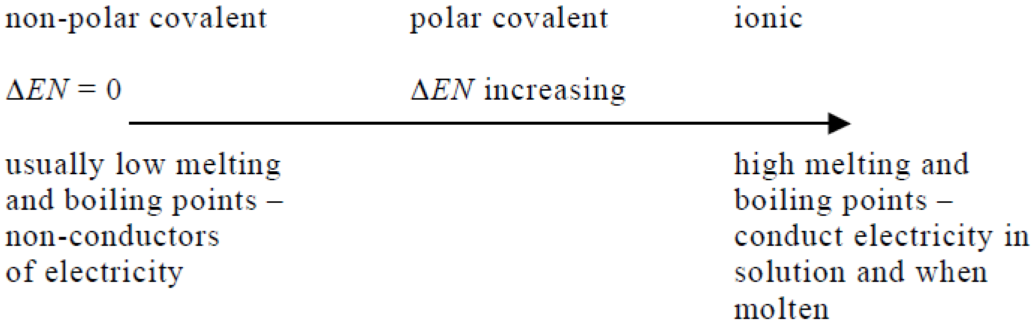
Shapes of molecules

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 ΔEN = difference in electronegativity values between the two atoms forming the bond.



non-polar covalent

$\Delta EN = 0$

usually low melting and boiling points – non-conductors of electricity

polar covalent

ΔEN increasing

ionic

high melting and boiling points – conduct electricity in solution and when molten

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_2O):

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 $\Delta EN = 3.5 - 2.2 = 1.3$

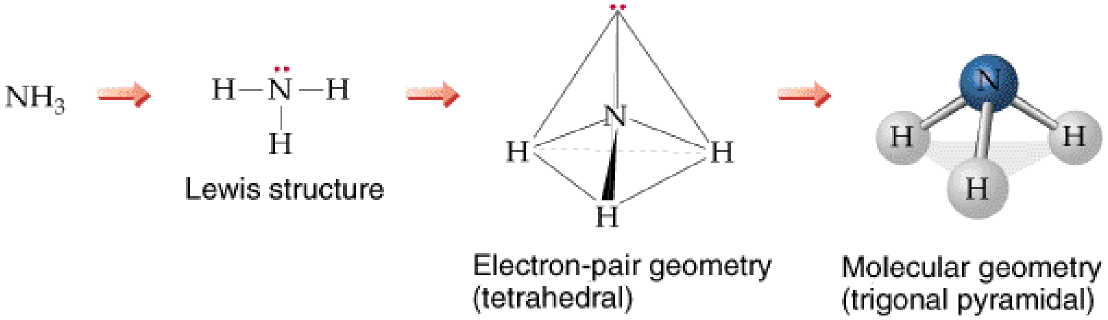
It might therefore be expected that both compounds will have the same type of bonding, most likely polar covalent.
However, sodium hydride is a solid at room temperature and when melted and electrolysed, hydrogen gas is produced at the positive electrode. This demonstrates that sodium hydride is ionic and also that it contains the hydride ion, H^-. 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_4^+) 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 upin 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_4 and XeF_4 may, at first sight, appear likely to be the same shape.

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

$$CF_4 = \frac{4 + 4}{2}$$

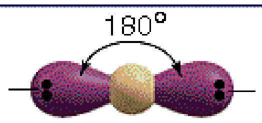
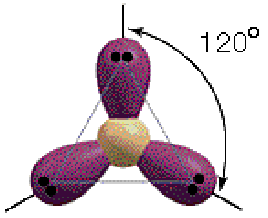
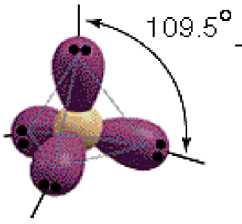
= 4 pairs.

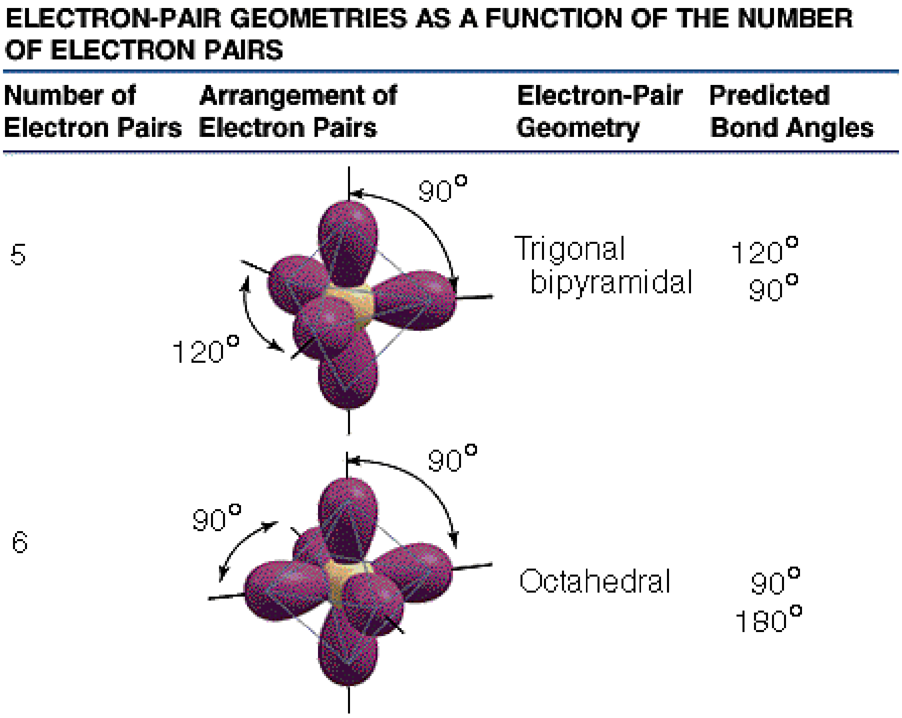
$$XeF_4 = \frac{8 + 4}{2}$$

= 6 pairs.

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

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

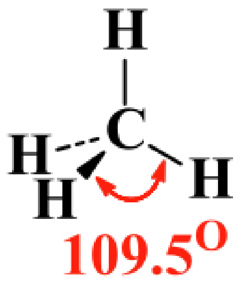
Number of Electron Pairs	Arrangement of Electron Pairs	Electron-Pair Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°

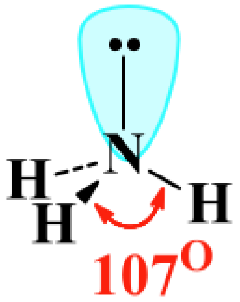


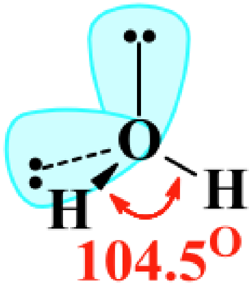
ELECTRON-PAIR GEOMETRIES AS A FUNCTION OF THE NUMBER OF ELECTRON PAIRS

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

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:

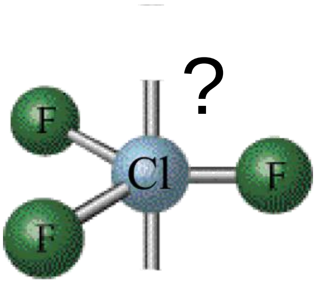


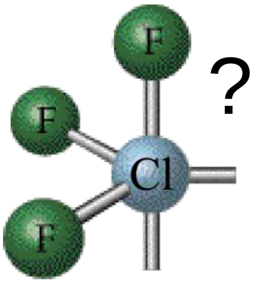


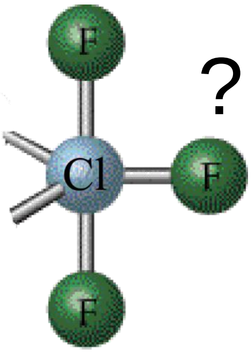


Since lone pairs repel more than bonding pairs, this leads to a wide range of shapes within different molecules:
Electron pair repulsions decrease in strength in the order:

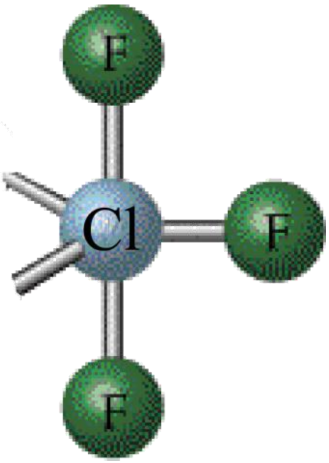
non-bonding/non-bonding
non-bonding/bonding
bonding/bonding





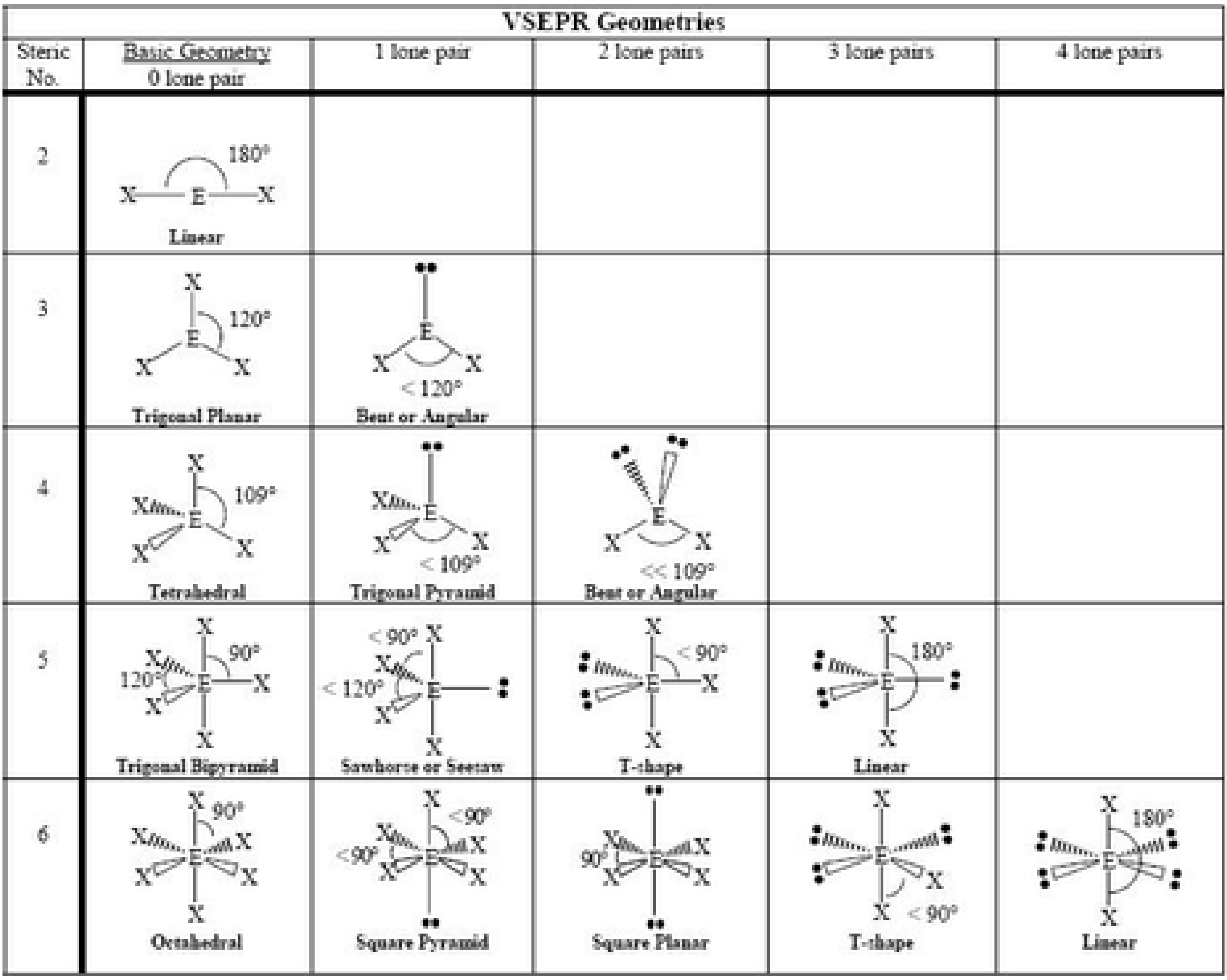


Placing the non-bonding lone pairs at the Axial positions would appear to give least repulsion but they would only be 90° away from the 3 bonding pairs. To minimize e^-– e^- repulsion, lone pairs are always placed in equatorial positions, so …



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

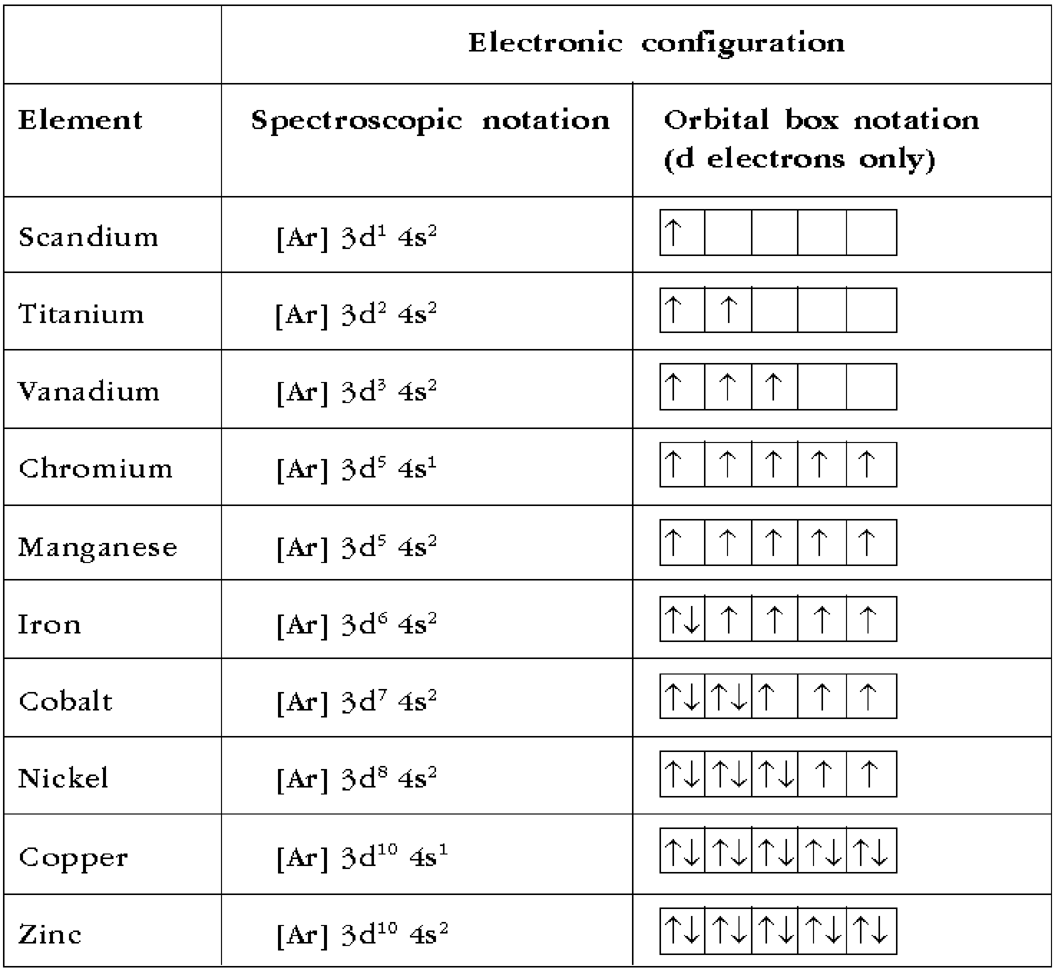


VSEPR Geometries

Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	180° Linear				
3	120° Trigonal Planar	< 120° Bent or Angular			
4	109° Tetrahedral	< 109° Trigonal Pyramid	<< 109° Bent or Angular		
5	90° 120° Trigonal Bipyramid	< 90° < 120° Sawhorse or Seesaw	< 90° T-shape	180° Linear	
6	90° Octahedral	< 90° < 90° Square Pyramid	90° Square Planar	< 90° T-shape	180° Linear

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).



	Electronic configuration	
Element	**Spectroscopic notation**	**Orbital box notation (d electrons only)**
Scandium	[Ar] $3d^1\ 4s^2$	[↑] [ ] [ ] [ ] [ ]
Titanium	[Ar] $3d^2\ 4s^2$	[↑] [↑] [ ] [ ] [ ]
Vanadium	[Ar] $3d^3\ 4s^2$	[↑] [↑] [↑] [ ] [ ]
Chromium	[Ar] $3d^5\ 4s^1$	[↑] [↑] [↑] [↑] [↑]
Manganese	[Ar] $3d^5\ 4s^2$	[↑] [↑] [↑] [↑] [↑]
Iron	[Ar] $3d^6\ 4s^2$	[↑↓] [↑] [↑] [↑] [↑]
Cobalt	[Ar] $3d^7\ 4s^2$	[↑↓] [↑↓] [↑] [↑] [↑]
Nickel	[Ar] $3d^8\ 4s^2$	[↑↓] [↑↓] [↑↓] [↑] [↑]
Copper	[Ar] $3d^{10}\ 4s^1$	[↑↓] [↑↓] [↑↓] [↑↓] [↑↓]
Zinc	[Ar] $3d^{10}\ 4s^2$	[↑↓] [↑↓] [↑↓] [↑↓] [↑↓]

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.

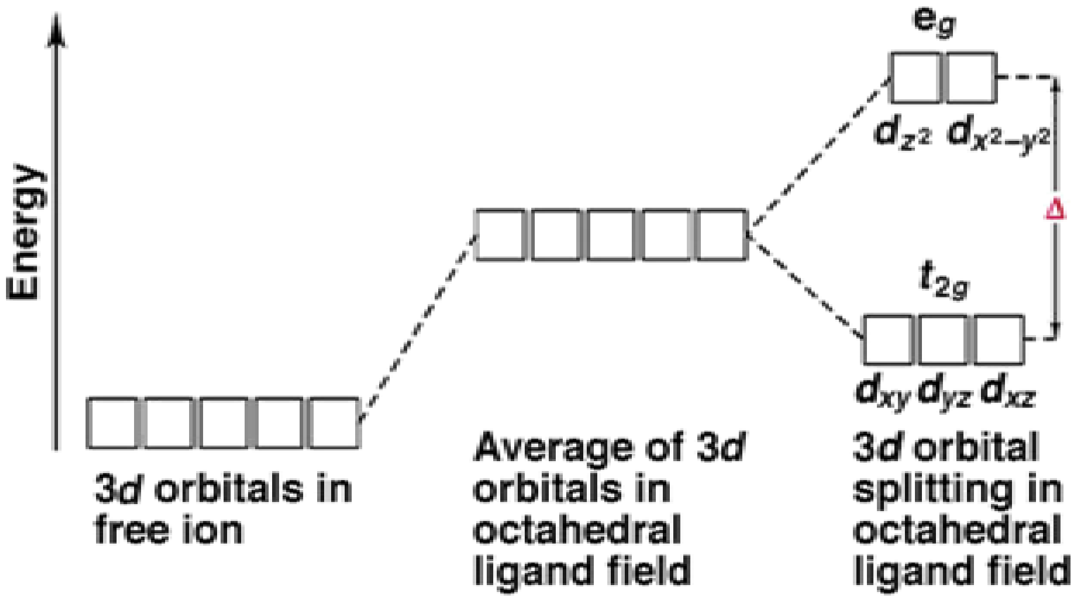
Colour in Transition Metal Compounds

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.

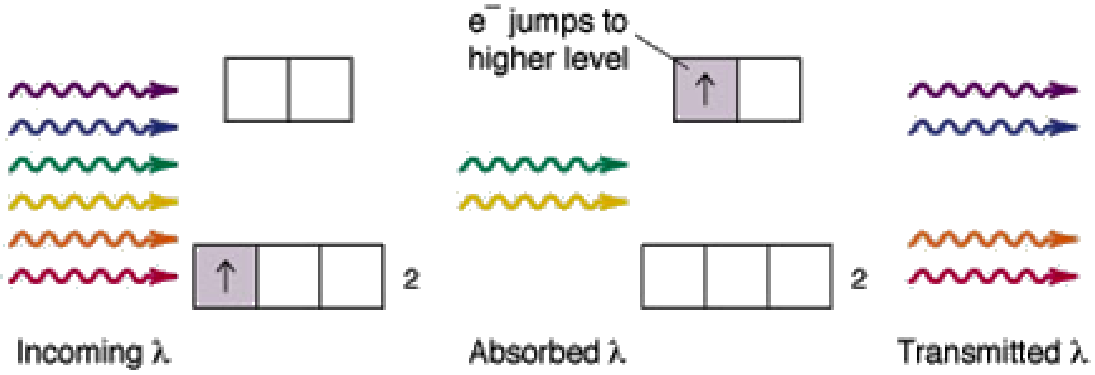
If blue light is absorbed, the colours transmitted are red and green, which is seen as yellow.

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).

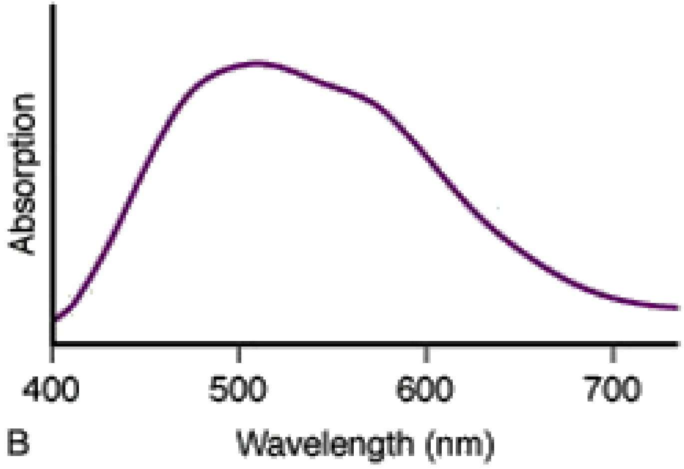


Different species (ligands) bonded to the central transition metal ion produce different splits in the d-orbitals, and it is the size of this split which determines the colour produced by the compound or complex.

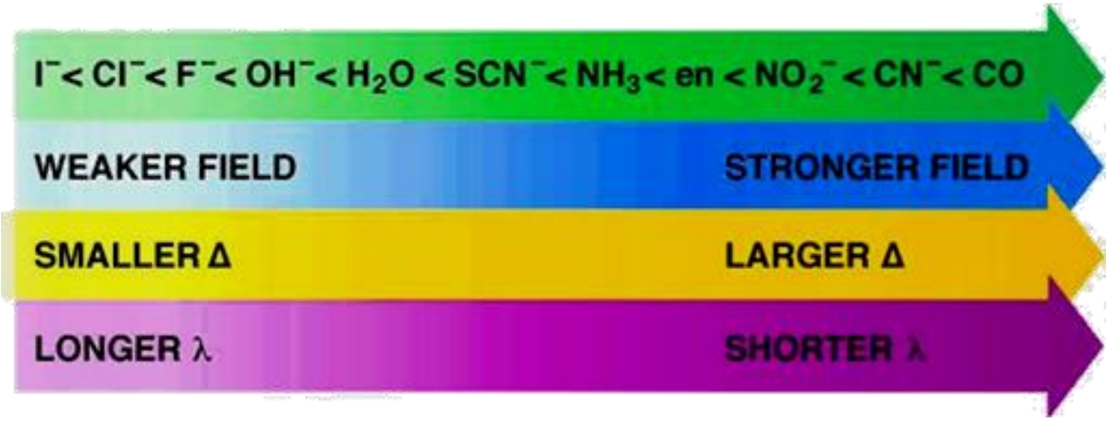
e.g in $[Ti(H_2O)_6]^{3+}$

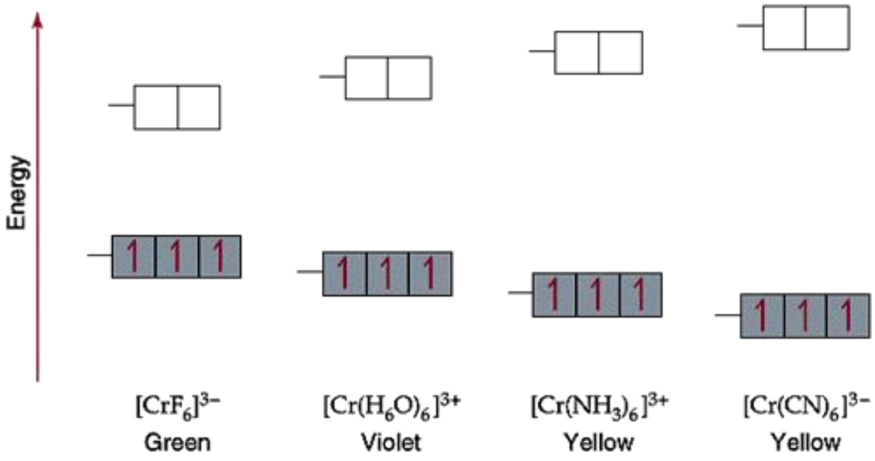


Green-yellow light is *absorbed* as an electron is promoted from one set of *d-orbitals* to the other set of *d-orbitals*.
d → d transitions. The blue & red light transmitted makes the compound a purple colour



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.

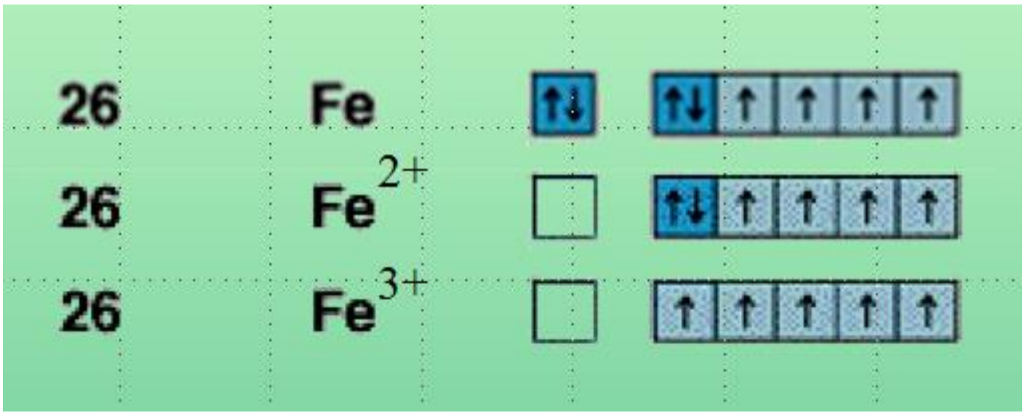
<u>Oxidation Number in Transition Metal Compounds</u>

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 4*s* electrons but some or all of their 3*d* electrons.

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



The Fe^{3+} ion forms in preference to 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 Na^+, K^+, 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 CrO_4^{2-} ?

Rule 2. We assume each oxygen is -2, so 4 *x* O = - 8

Rule 5. Overall charge on ion is -2, so Cr must be +6 .

What is the oxidation number for Cr in $Cr_2O_7^{2-}$?

Rule 2. We assume each oxygen is -2, so 7 *x* O = - 14

Rule 5. Overall charge on ion is -2, so 2 *x* 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.

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

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

e.g. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

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

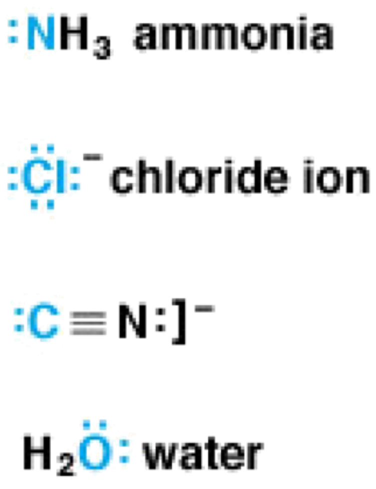
e.g. $Fe(OH)_2 + OH^- \rightarrow Fe(OH)_3 + e^-$

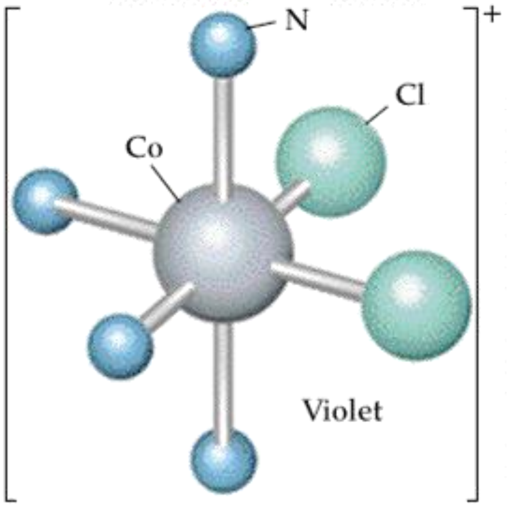
Oxidation results in an increase in the oxidation number whereas reduction results in a decrease in the oxidation number.

Transition Metal Complexes and Names

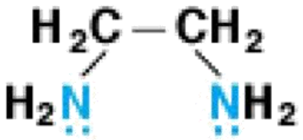
A transition metal complex is a ***Metal*** (atom or ion), ***surrounded by ligands***, with the ligands bound to the metal through ***coordinate covalent*** bonds. The ligand is an atom, molecule or ion that contains at least one ***lone pair***.

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

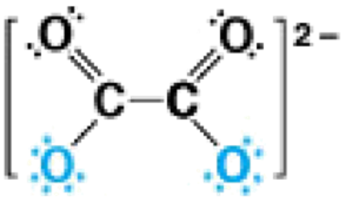




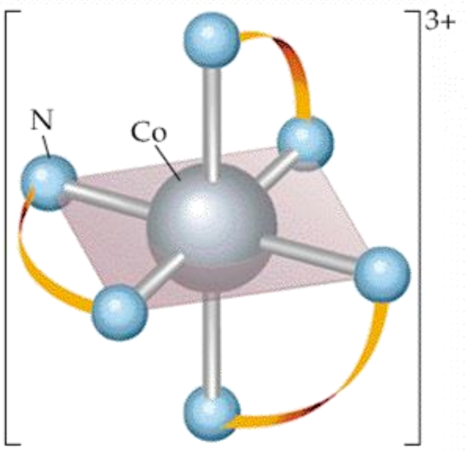
Bidentate ligands: Can form ***two bonds*** with the metal atom/ion



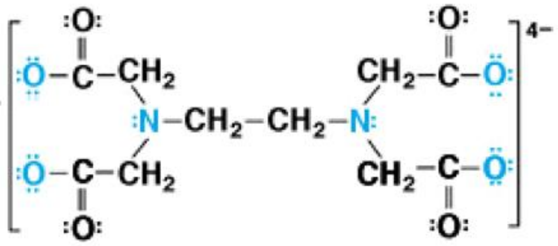
ethylenediamine (en)



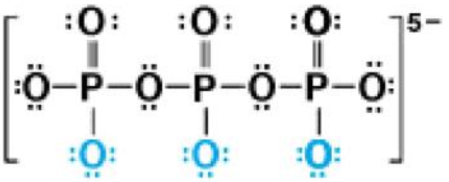
oxalate ion



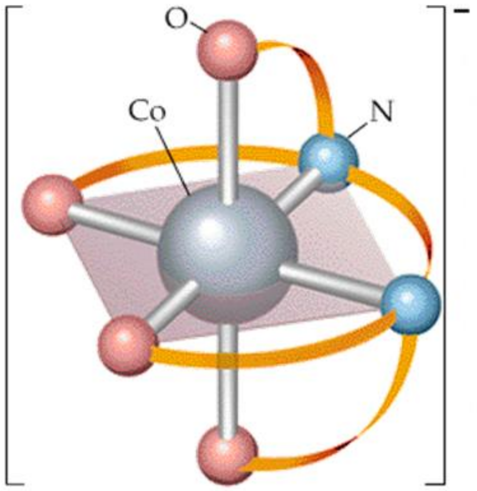
Polydentate ligands: Can form ***many bonds*** with the metal atom/ion:



ethylenediaminetetraacetate (EDTA) ion



triphosphate ion



Naming Complexes

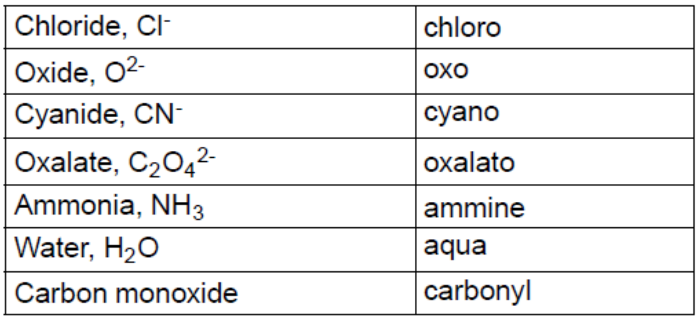
1. **To name a complex salt (containing positive and negative ion), use the normal chemistry rules i.e. name the positive ion first, then the negative ion. To do this, we need to know the rules for naming the complex ion:**

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 MnO_4^- are often written without brackets. The metal symbol is written first, then the negative ligands followed by the neutral ligands, e.g. $[Fe(OH)_2(H_2O)_4]^+$.

2. **The name of the complex part has two parts written as one word. The ligands are named first and the central metal ion second.**
3. **Give the ligand name and the number of each (di-, tri-, etc). (see a below)**
4. **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.**
5. **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)**

a) When naming the complex ion or molecule the ligands should be named first, in alphabetical order, 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, Cl^-, becomes chloro, cyanide, CN^-, becomes cyano. If the ligand is a negative ion the name of which ends in -ite, the final 'e' changes to 'o', e.g. nitrite, NO_2^-, changes to nitrito.



Chloride, Cl^-	chloro
Oxide, O^{2-}	oxo
Cyanide, CN^-	cyano
Oxalate, $C_2O_4^{2-}$	oxalato
Ammonia, NH_3	ammine
Water, H_2O	aqua
Carbon monoxide	carbonyl

b) 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 $Na_3[Co(F)_6]$

1. The positive ion name precedes the negative ion name. So the correct name will be sodium........then the complex ion.
2. Name the ligand then the metal in the complex ion.
3. Six fluoride ligands gives '**hexafluoro-**'.
4. The next step is find out the oxidation number of cobalt in **$Na_3[Co(F)_6]$**

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.

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

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

Questions:

Name the following complexes:

(a) $[CoCl_4]^{2-}$

(b) $[Ni(H_2O)_6]^{2+}$

(c) $[Fe(CN)_6]^{4-}$

(d) $[Ti(NH_3)_6]^{3+}$

(e) $[Ni(CN)_6]^{4-}$

(f) MnO_4

(g) $[PtCl_6]^{2-}$

Dynamic Equilibrium

Revision

Dynamic equilibrium happens in a closed system when the rate of reverse reaction equals rate of forward reaction. The composition of reactants and products appears to stay constant.

Homogenous: all species in the same phase

Heterogenous : species in more than one phase

Equilibrium constant

The equilibrium constant (K) is expressed in terms of concentration (or pressure for gases) .

For the reaction:

$aA + bB \rightarrow cC + dD$

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Concentrations of pure solids or liquids are constant and are given the value 1, thus

$S(s) + O_2(g) \rightarrow SO_{2(g)}$ $K = \frac{[SO_2]}{[O_2]}$

Equilibrium constant is for a given temperature and is **independent of concentration, pressure or the presence of a**

catalyst. The effect of changes in concentration can be explained in terms of a fixed equilibrium constant. K has no units - it is dimensionless.

e.g. When dilute hydrochloric acid is added to a yellow solution of sodium chromate the solution turns orange:

$2CrO_4^{2-(}aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$
Yellow orange

The added H^+(aq) ions increase the rate of the forward reaction compared to the reverse reaction. This continues until the rates of the forward and reverse reactions are the same and equilibrium is re established.

The position of the equilibrium has moved to the right. Overall the increase in the concentration of H^+(aq) is compensated for by a decrease in the concentration of CrO_4^{2-} ions and an increase in the concentration of $Cr_2O_7^{2-}$ ions and H_2O molecules, thus keeping the value of *K* the same:

$$K = \frac{\left[Cr_2O_7^{\ 2-}\right]}{\left[CrO_4^{\ 2-}\right]^2\left[H^+\right]^2}$$

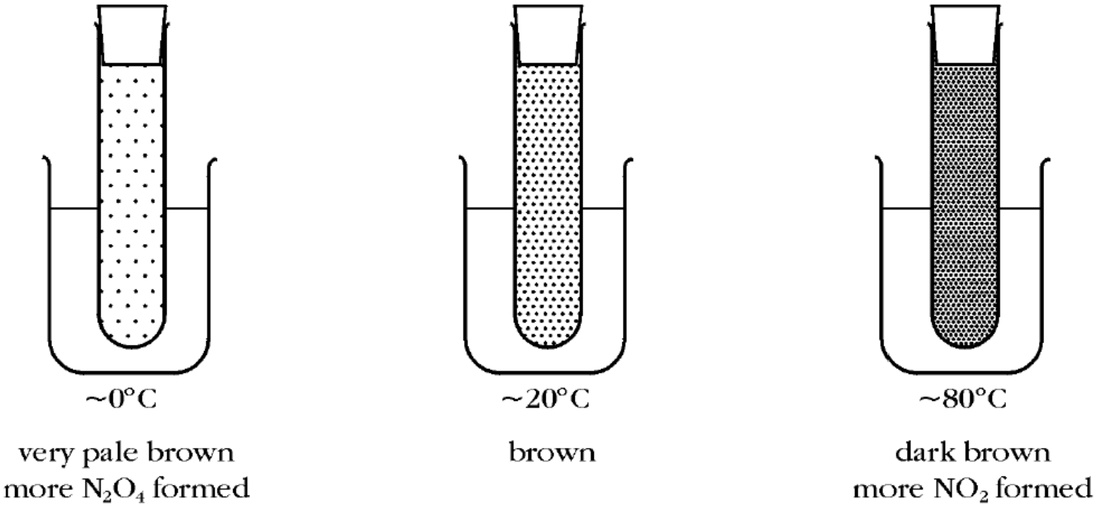
This fact is stated formally in Le Chatelier's principle, which states that 'when a reaction at equilibrium is subjected to change, the composition alters in such a way as to minimise the effects of the change'.

The effect of changing temperature

The effect of a temperature change on a reaction in equilibrium can be demonstrated in the laboratory using the following example:

N_2O_4 (*g*) ⇌ $2NO_2$ (*g*) ΔH = +ve
yellow brown

Three boiling tubes filled to an equal colour intensity with this gas mixture are collected at room temperature. One is placed in ice water (~0°C) and one in hot water (~80°C) while the third is kept, as a control, at room temperature (Figure 3). The three tubes are left for about five minutes and the colour intensities are then compared.



From the colour changes that have taken place, it is evident that the relative concentrations of N_2O_4 and NO_2 have been changed by a change in temperature. This means that the actual value of *K* has changed. Equilibria are therefore temperature dependent. In fact most equilibrium constants are quoted at a specific temperature.

The equilibrium constant is:

$$K = \frac{[NO_2]^2}{[N_2O_4]}$$

The reaction is endothermic for the forward reaction and exothermic for the reverse. The colour change from 20°C to 0°C shows that more N_2O_4 is formed at 0°C and therefore $[N_2O_4]$ increases and $[NO_2]$ decreases. This leads to a fall in the value of K.

Similarly, the colour change from 20°C to 80°C shows that more NO_2 is formed at 80°C and therefore $[NO_2]$ increases and $[N_2O_4]$ decreases. This leads to a rise in the value of K. These observations can be related to the ΔH value and are summarised in the following way.

For endothermic reactions a rise in temperature causes an increase in K while for exothermic reactions a rise in temperature causes a decrease in K.

K and Equilibrium Position

A high value of K means that the fraction used to calculate it is 'top heavy' so there is more product, i.e. equilibrium lies to the right. The table below summarises this for different reactions:

System	**Value of K**	**Position of equilibrium**
$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$	1.7×10^7 at 25°C	Because $K >> 1$ the equilibrium lies to the right
$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$	1.8×10^{-5} at 25°C	Because $K << 1$ the equilibrium lies to the left
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	0.87 at 55°C	Because $K \approx 1$ the equilibrium lies to neither the left nor the right

Effect of a Catalyst

Remember that all a catalyst does is lower activation energy. This will be true for forward and reverse reactions, so a catalyst speeds up the rate of establishment of equilibrium. It doesn't affect the position of equilibrium; therefore it must have no effect on K.

Questions:

1. **The value for the equilibrium constant, K, for a specific example of the following reaction is equal to 1:**

   acid + alcohol ⇋ ester + water

a) i) Predict the maximum yield of ester, given this value of K.

ii) Give ***one*** reason why this yield might not be achieved in practice.

b) A student suggested that a careful choice of catalyst could increase the yield of ester. Comment on this suggestion.

c) Another student suggested that increasing the concentration of the alcohol in the reaction mixture would increase the yield of ester by altering the value of K. Comment on this suggestion.

2. **The balanced equation for the principle reaction in the contact process is:**

   $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)\ \Delta H = -ve$

a) Write an expression for K, the equilibrium constant for this reaction, when the system has reached equilibrium.

b) i) State Le Chatelier’s Principle.

ii) Use this generalisation to predict how an increase in temperature would affect the position of equilibrium.

iii) Explain the effect this increase in temperature would have on the value of K.

Acid/Base Equilibria

From the National 5 course it will be remembered that the pH of an aqueous solution is a measure of the concentration of hydrogen ions in the solution. In fact the pH of any aqueous solution can be calculated using the expression:

$pH = -\log[H^+]$

The following examples illustrate its use:

pure water $[H^+] = 10^{-7}$ so pH = 7

1.0 mol l^{-1} HCl $[H^+] = 1.0\ (10^0)$ so pH = 0

0.2 mol l^{-1} HCl $[H^+] = 0.2\ (2 \times 10^{-1})$

So $pH = -\log 2 - \log(10^{-1})$

$= -0.3 + 1.0 = 0.7$

For calculations involving strong acids and alkalis it can be assumed that they are 100% dissociated and that the small number of hydrogen ions supplied by the water can be ignored.

In S4, acids were defined as producing hydrogen ions in solution and bases as producing hydroxide ions in solution. These two ions combine in the neutralisation equation:

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

However, this definition is simplistic and can't explain all acids. For example, pure hydrogen chloride is a gas that contains no H^+ ions and ammonia has no OH^- ions but can neutralise an acid. It was also discovered that the H^+ ion could not exist in aqueous solution. The H^+ ion is so small that the electric field it creates is huge and in water it attracts a lone pair of electrons to form H_3O^+, which is called the hydronium ion.

$H^+(aq) + H_2O(l) \rightarrow H_3O^+(aq)$

The shorthand $H^+(aq)$ is always used in stoichiometric and equilibrium equations, although this is not strictly accurate. In 1923 the new discoveries led two chemists, Brønsted and Lowry, to define acids and bases in a different way:

An acid is any substance capable of donating a proton.

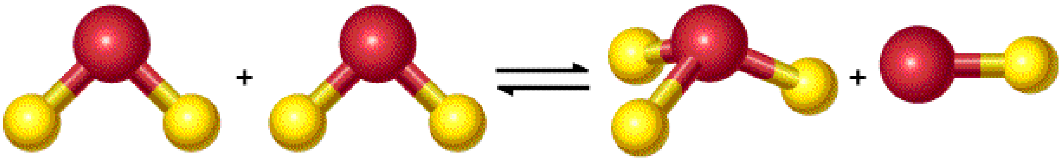
A base is any substance capable of accepting a proton.

The dissociation of water

In Brønsted–Lowry terms the ionisation of water is represented by:

$H_2O(l) + H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$

acid + base conjugate acid + conjugate base



The equilibrium constant is :

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Since water is a liquid, $[H_2O] = 1$ (see page 37), giving:

$$K = [H_3O^+][OH^-]$$

This particular equilibrium constant is known as the **ionic product** (Kw) for water and has the value of 1.0×10^{-14} at 25°C.

The water equilibrium is more usually written as:

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ and $Kw = [H^+][OH^-]$

In **pure** water, for every molecule which ionises, one H+ and one OH^- ion are produced, hence the $[H^+]$ in mol l^{-1} must equal the $[OH^-]$ in mol l^{-1}, i.e. the number of H^+ and OH^- ions in water are equal.

Substitution of $[OH^-]$ by $[H^+]$ in the above equilibrium expression gives:

$[H^+]^2 = 10^{-14}$ mol^2 l^{-2}

taking square roots $[H^+] = 10^{-7}$ mol l^{-1}

so also $[OH^-] = 10^{-7}$ mol l^{-1}

$$Kw = [H^+][OH^-] = 1.0 \times 10^{-14}$$

This relationship can be used to calculate the pH of an alkali as shown:

0.01 mol l^{-1} NaOH $[OH^-] = 10^{-2}$, $[H^+] = 10^{-12}$, pH = 12

0.5 mol l^{-1} NaOH $[H^+] = 2 \times 10^{-14}$ pH = $-\log 2 - \log(10^{-14})$

$= -0.3 + 14 = 13.7$

Kw is always quoted as 1.0 × 10^{-14} at 25°C since the value varies with temperature:

$H_2O(l) \rightleftharpoons H^+(aq) + OH–(aq)$ ΔH +ve

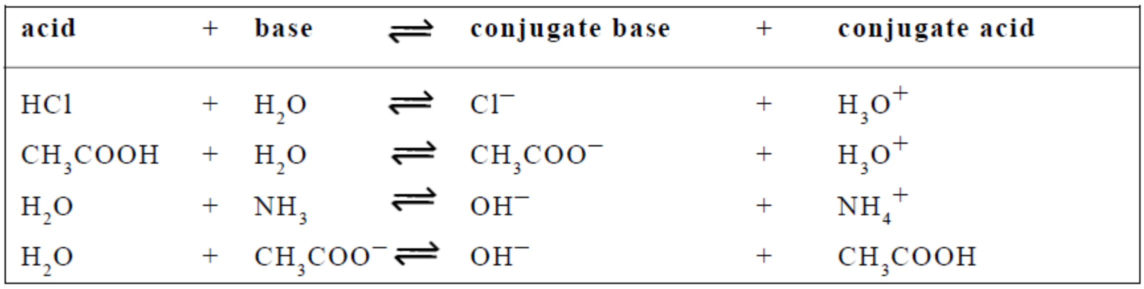
As the reaction is endothermic, an increase in temperature moves the equilibrium to the right and a decrease moves it to the left.

Questions

Calculate the pH of the following solutions:
(a) 0.35 mol l–1 HNO_3
(b) 0.14 mol l–1 H_2SO_4 (assume fully ionised)
(c) 0.78 mol l–1 NaOH

Conjugate Acids and Bases

When an acid donates a proton the species left is called the conjugate base of that acid. When a base accepts a proton the species formed is called the conjugate acid of that base.



acid	+	base	⇌	conjugate base	+	conjugate acid
HCl	+	H_2O	⇌	Cl^-	+	H_3O^+
CH_3COOH	+	H_2O	⇌	CH_3COO^-	+	H_3O^+
H_2O	+	NH_3	⇌	OH^-	+	NH_4^+
H_2O	+	CH_3COO^-	⇌	OH^-	+	CH_3COOH

This table also illustrates the **amphoteric** nature of water since it can act both as a proton acceptor and a proton donor.

What is a 'Strong' Acid?

The strongest common acids are HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, and H_2SO_4. All strong acids dissociate completely in solution:

$$HNO_{3(aq)} \rightleftharpoons H^{+}_{(aq)} + NO^{-}_{3\,(aq)}$$

Therefore, the pH depends only on the initial molarity of the acid.

The strongest common <u>bases</u> are oxides and hydroxides of Group I metals. All strong bases dissociate completely in solution:

$$O^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons 2OH^{-}_{(aq)}$$

Bases do not need to include OH^- ions:

$$H^{-}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_{2(g)} + OH^{-}_{(aq)}$$
$$N^{3-}_{(aq)} + 3H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + 3OH^{-}_{(aq)}$$

Therefore, the $[OH^-]$, and hence the $[H^+]$ and pH, depends only on the initial molarity of the base.

Dissociation and strength

The dissociation of any acid, HA, in aqueous solution can be represented by the equation:

$HA(aq)$ +	$H_2O(l)$ →	$H_3O^+(aq)$ +	$A^-(aq)$
acid	base	conjugate acid	conjugate base

The dissociation constant of acid HA is a measure of the strength of the acid. It is simply the equilibrium constant from the above equation and is:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The $[H_2O]$ has been omitted as it is the solvent and taken to be 1.

In **strong acids** the above equilibrium lies to the right with effectively complete dissociation so that *K*a has no meaning. However, some acids do not dissociate well (less than 5%) in aqueous solution and these are called **weak acids**.

Conveniently, nearly all acids fall into one of these two categories. Within the weak acids, the value of *K*a gives a measure of how weak (or how dissociated) the acid is: the smaller the value of *K*a, the weaker the acid. A similar constant, K_b exists for the base equilibrium, but in general K_a is used to calculate pH for both acids and bases – we will see how this is done later.

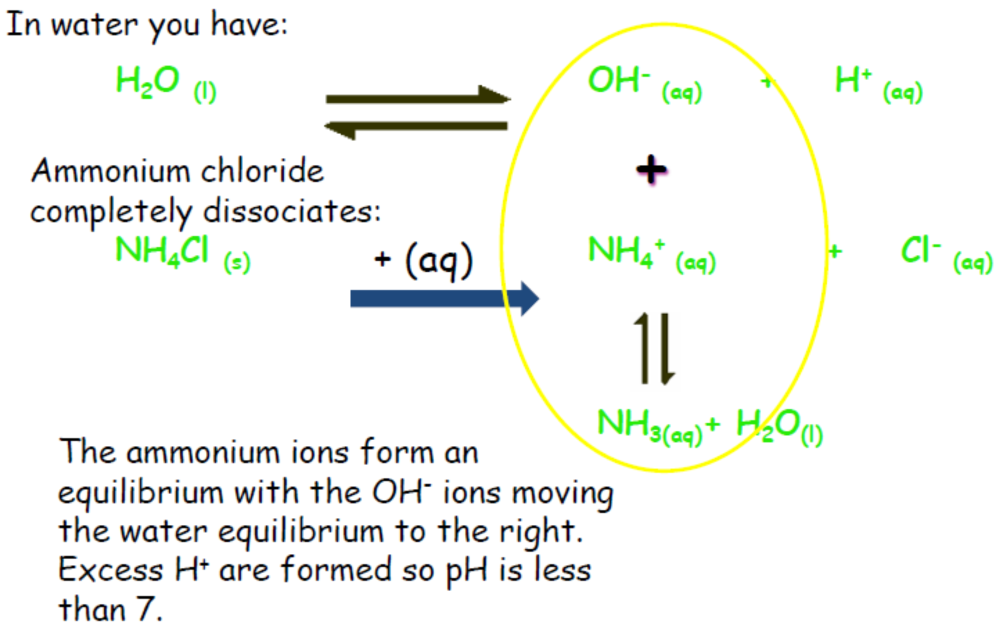
pH of Salt Solutions

The **pH of a salt** solution depends on the **strength** of the **acid** and **base** from which it was formed.

Acid	Base	pH of salt
Strong	Weak	Acidic
Strong	Strong	Neutral
Weak	Strong	Alkaline

All salts are **strong electrolytes** and completely dissociate in solution. The ions of a **weak acid** or **base** when dissolved will set up an equilibrium with the ions in water.

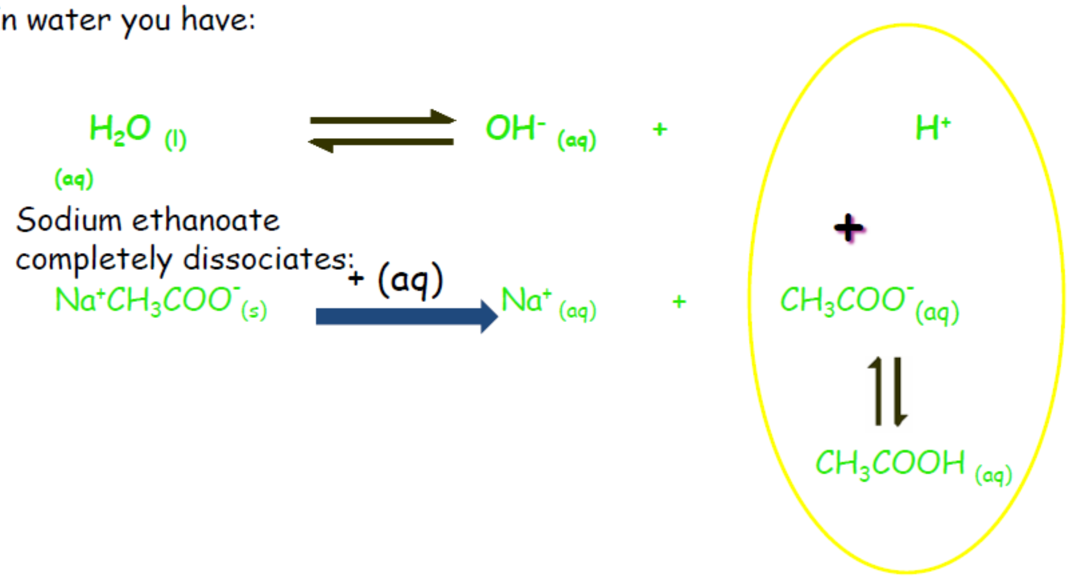
Acidic Salt



The ammonium ions form an equilibrium with the OH^- ions moving the water equilibrium to the right. Excess H^+ are formed so pH is less than 7.

Alkaline Salt

In water you have:



The ethanoate ions form an equilibrium with the H^+ ions moving the water equilibrium to the right.

Excess OH^- ions are formed so the pH is greater than 7.

Calculating pH for a weak acid

Using the equilibrium constant (dissociation constant) from the reaction on page 47, the pH of a weak acid can be calculated:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$\text{Since } [H_3O^+] = [A^-]$$

$$K_a = \frac{[H_3O^+]^2}{[HA]}$$

Taking logs of both sides:

$$\begin{aligned}\log K_a &= \log[H_3O^+]^2 - \log[HA]\\ &= 2\log[H_3O^+] - \log[HA]\end{aligned}$$

but $-\log[H_3O^+] = \text{pH}$, and assigning $-\log K_a$ as $\text{p}K_a$ we get:

$$\begin{aligned}-\text{p}K_a &= -2\text{pH} - \log[HA]\\ \text{p}K_a &= 2\text{pH} + \log[HA]\end{aligned}$$

For a weak acid HA of concentration *c* mol l^{-1}, [HA] at equilibrium will be approximately equal to the original concentration *c* mol l^{-1}, so:

$$\text{p}K_a = 2\text{pH} + \log c$$

Rearranging for pH:

$$\boxed{\text{pH} = \tfrac{1}{2}\text{p}K_a - \tfrac{1}{2}\log c}$$

Questions

1. Calculate the pH of a 0.2 mol l^{-1} solution of ethanoic acid if $Ka = 1.7 \times 10^{-5}$

2. 0.02 mol l^{-1} benzoic acid C_6H_5COOH, a monobasic acid, was found to have a pH of 2.94. Calculate the *Ka* of this weak acid.

Buffer solutions

A buffer solution is one in which the pH of the solution remains approximately constant when small amounts of acid or base are added or the solution is diluted with water.

An **acidic buffer** consists of a solution of a weak acid and one of its salts with a strong alkali. A **basic buffer** consists of a solution of a weak base and one of its salts with a strong acid. Both types of buffer solution work in the same way.

In an acid buffer solution, the weak acid supplies more hydrogen ions when the existing ones are removed by a base being added, while the salt of the weak acid provides the conjugate base to react with the hydrogen ions when small amounts of acid are added.

In a basic buffer solution, the weak base reacts with the hydrogen ions when acid is added and the salt provides the conjugate acid, which dissociates to replace the hydrogen ions when these are removed by addition of small amounts of base.

In consequence, the pH hardly changes in both cases. This principle is illustrated by an acid buffer of weak acid HA and the sodium salt of that acid NaA. In solution the following occurs:

$$\mathrm{HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)} \quad \text{equilibrium}$$

$$\text{and} \quad \mathrm{NaA(aq) \rightarrow Na^+(aq) + A^-(aq)} \quad \text{fully ionised}$$

Addition of small volumes of H^+ does not alter the pH greatly since an increase in $[H^+]$ favours the reverse reaction (HA formation) to maintain K_a. Since $[A^-]$ is high compared to $[H^+]$ in the original buffer solution, its ability to remove H^+ ions is substantial (but not infinite) and the pH of the solution is maintained.

In the same way, addition of OH^- does not alter the pH greatly since the OH^- ions combine with the H^+ of the weak acid until K_w is attained. Removal of H^+ means that more HA ionises, giving $H^+ + A^-$ until equilibrium is re-established, and the pH of the solution is maintained:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$[H_3O^+] = \frac{[K_a][HA]}{[A^-]}$$

where [HA] is the concentration of the acid as it is a weak acid and $[A^-]$ is the concentration of the salt as it is fully ionised and very little comes from the acid dissociating. Therefore:

$$[H_3O^+] = \frac{K_a[\text{acid}]}{[\text{salt}]}$$

If the buffer solution has water added to it, i.e. it is diluted, both [acid] and [salt] are equally affected and therefore $[H_3O+]$ and the pH remain unaltered.

An efficient buffer must have a reasonable reserve of HA and A^- as the H^+ from HA removes added OH^- and the A^- removes added H^+. If [acid] = [salt] the buffer will have the same ability to resist addition of H^+ and OH^-.

Similar reasoning can be used to show how a basic buffer solution operates. The pH of an acid buffer solution can be calculated by conversion of the above equation,

$$\boxed{\mathrm{pH} = \mathrm{p}K_a - \log\frac{[\mathrm{acid}]}{[\mathrm{salt}]}}$$

Questions

1. Calculate the pH of the buffer solution made from 1.0 mol l^{-1} methanoic acid and 1.78 mol l^{-1} sodium methanoate solution. The pK_a of methanoic acid is 3.8.

2. Calculate the pH of the buffer solution made from 0.1 mol l^{-1} solution of ethanoic acid and potassium ethanoate. The pK_a of ethanoic acid is 4.8.

Indicators

Indicators are used to determine the end-point in an acid–alkali titration. A suitable indicator must be chosen for any given reaction. Indicators are dyes whose colours are sensitive to pH. An indicator is usually a weak acid that dissociates as shown:

$$\mathrm{HIn(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{In^-(aq)}$$

The unionised form of the indicator (HIn) has a different colour from its conjugate base (In^-). The equilibrium constant (K_{In}) for the above equation is:

$$K_{\mathrm{In}} = \frac{[\mathrm{H_3O^+}][\mathrm{In^-}]}{[\mathrm{HIn}]}$$

Rearranging this expression gives:

$$\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]} = \frac{\mathrm{K}_{\mathrm{In}}}{[\mathrm{H}_3\mathrm{O}^+]}$$

This shows that the ratio of the two coloured forms is a function of the H_3O^+ concentration, i.e. the pH of the solution. It follows therefore that the colour of the indicator in any given solution depends on the relative concentrations (ratio) of the two coloured forms, which in turn is determined by the pH.

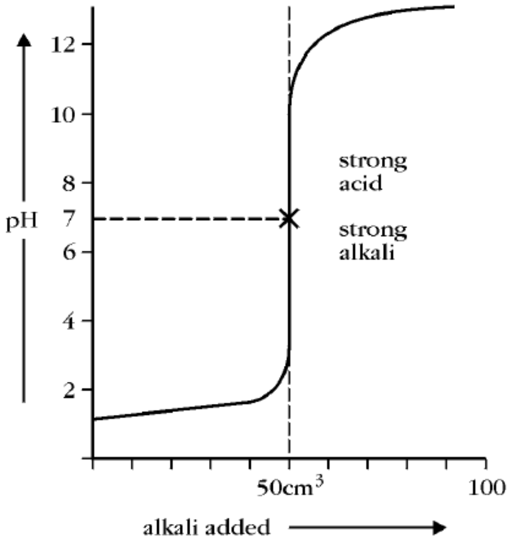
The theoretical point at which the colour change occurs is when [HIn] = [In–] and therefore KIn = $[H_3O^+]$. In other words, the colour change occurs when pKIn = pH. In practice the colour change cannot be seen when[HIn] = $[In^-]$ and it is only distinguishable when [HIn] and $[In^-]$ differ by a factor of 10.

The pH range over which a colour change can be seen is therefore established using the expression:

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{In}} \pm 1 \qquad (\log 10 = 1)$$

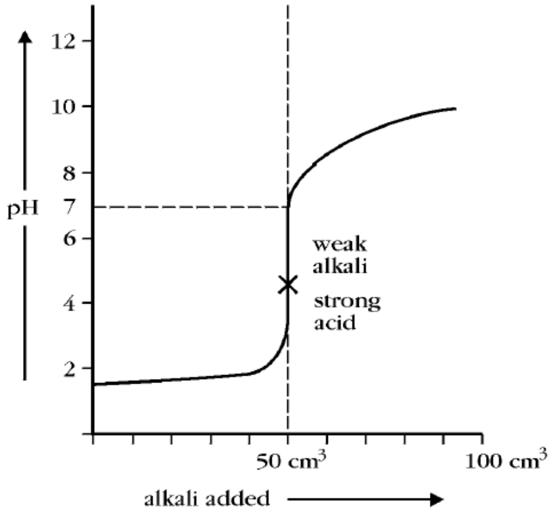
The appropriate indicator for any titration must be chosen such that the colour change occurs over the pH range when the pH is changing very rapidly. This means that the indicator must change colour during the addition of, say, half a drop of reagent. The indicator for a reaction can therefore be chosen by reference to titration curves, which are drawn from data obtained by measuring the pH of an acid continuously against the volume of alkali added during and after neutralisation.

Strong Acid + Strong Alkali



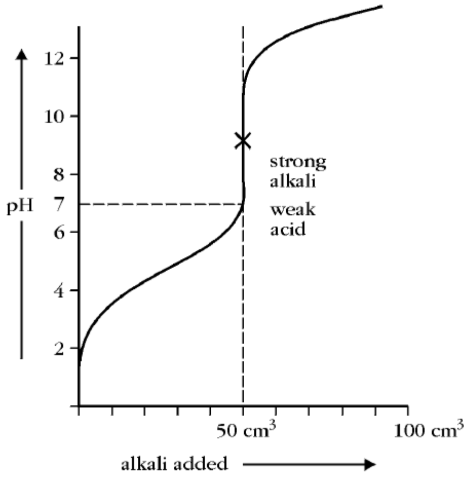
Note the rapid rise in pH as the end-point of the titration is approached. Thereafter the alkali added has nothing to react with and the pH continues to rise to a final value of 12. There is a region of rapid pH change around the end-point. For an indicator to be suitable, its pH range must fall within this region. It can be seen that for a strong acid and strong alkali a suitable indicator can have a colour change within the pH range 3–10.

Strong Acid + Weak Alkali



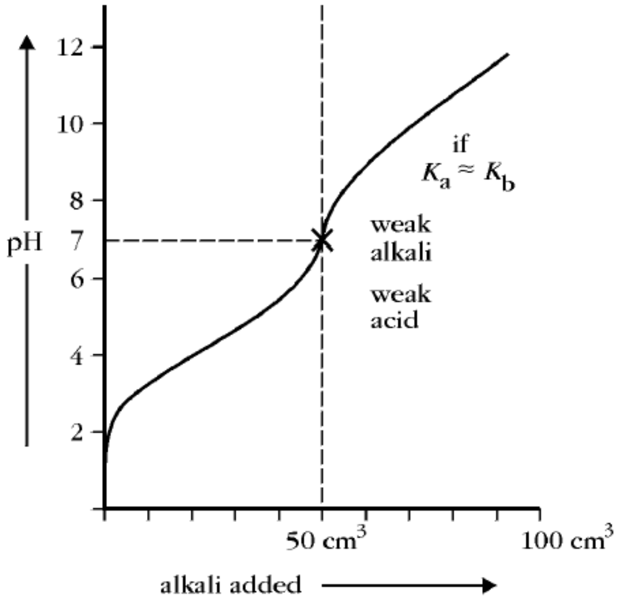
For a strong acid and weak alkali would change somewhere in the range 3–7.

Weak Acid + Strong Alkali



For a weak acid and strong alkali, a suitable indicator must change colour within the pH range 7–10.

Weak Acid + Weak Alkali



It is not possible to select any suitable indicator for a weak acid/weak alkali combination since the pH does not change rapidly enough at the end-point, i.e. the titration curve does not have an almost vertical section like the others.

The table below shows some common indicators, their pH range and colours.

Name of indicator	pH of colour change	Colour (HIn)	Colour (In)
Methyl orange	3.0–4.4	Orange	Yellow
Methyl red	4.2–6.3	Red	Yellow
Bromothymol blue	6.0–7.6	Yellow	Blue
Phenolphthalein	8.0–9.8	Colourless	Red

Question

From the table, calculate the p*Ka* and *Ka* for the four indicators.

Thermochemistry

Thermochemistry is the study of energy changes in reactions. **The First Law of Thermodynamics states that the total energy of the universe is constant** – energy can nether be created nor destroyed. Therefore, it only changes between different TYPES of energy.

Enthalpy changes are defined as the measured heat energy changes occurring during a reaction, usually per mole of product formed or reactant used up, depending on the particular enthalpy change being defined. The units are in kilojoules per mole, kJ mol^{-1}. From Higher, you will already be aware of standard enthalpy of combustion and the use of standard reaction enthalpies and standard bond enthalpies in the context of Hess's Law.

The standard enthalpy change is defined as the enthalpy change measured under standard conditions. Standard conditions are one mole of a substance at one atmosphere pressure and any specified temperature (in Kelvin). The symbol used is ΔH^o. The temperature specified is usually 298 K (25°C).

The standard state of a substance is the most stable state of that substance under standard conditions. **The standard enthalpy of formation (ΔH^o_f) of a compound is the enthalpy change when one mole of a compound is formed from its elements in their standard states.** The standard enthalpy of formation of elements is by definition zero, giving a base line from which enthalpy changes can be measured.

The standard enthalpy change for any reaction can be calculated from the standard enthalpies of formation of the substances in the equilibrium using the equation:

$$\Delta H^\circ = \Sigma\Delta H^\circ_f \text{ products} - \Sigma\Delta H^\circ_f \text{ reactants}$$

Example:

Calculate the standard enthalpy of reaction for the decomposition of copper(II) nitrate from the given standard enthalpies of formation.

Step 1: Write the equation with ΔH°_f values beneath each substance:

$$\begin{array}{lccccccc} & \text{Cu(NO}_3)_2\text{(s)} & \rightarrow & \text{CuO(s)} & + & 2\text{NO}_2\text{(g)} & + & \tfrac{1}{2}\text{O}_2\text{(g)} \\ \Delta H^\circ_f/\text{kJ mol}^{-1} & -307 & & -155 & & +34 & & 0 \end{array}$$

Step 2: Multiply each ΔH°_f value by its mole relationship:

$$\begin{array}{ccccccc} \text{Cu(NO}_3)_2\text{(s)} & \rightarrow & \text{CuO(s)} & + & 2\text{NO}_2\text{(g)} & + & \tfrac{1}{2}\text{O}_2\text{(g)} \\ -307 & & -155 & & +68 & & 0 \end{array}$$

Step 3: Use the equation $\Delta H^\circ = \Sigma\Delta H^\circ_f$ products – $\Sigma\Delta H^\circ_f$ reactants:

$$\begin{aligned} \Delta H^\circ &= \Sigma\Delta H^\circ_f \text{ prod} - \Sigma\Delta H^\circ_f \text{ reactants} \\ &= -155 + 68 - (-307) \\ &= -87 + 307 \\ &= +\ 220 \end{aligned}$$

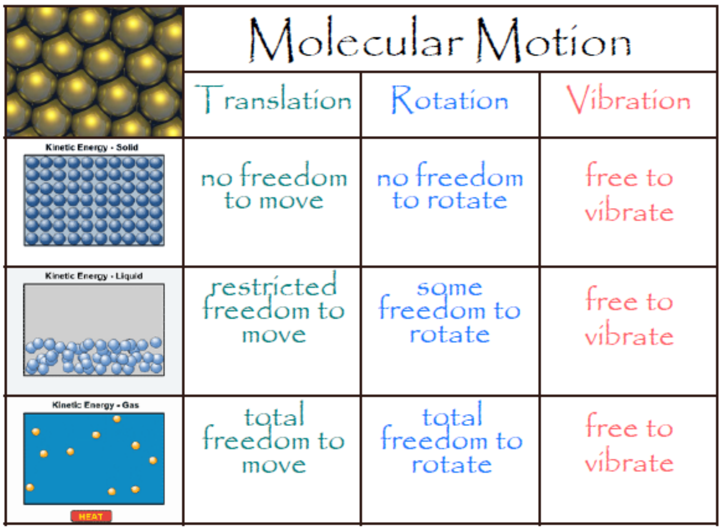
ΔH° for the reaction = +220 kJ mol^{-1}

Thermodynamics

Thermodynamics is concerned with the feasibility of a reaction i.e. whether a reaction will happen spontaneously or not. Increasingly we consider all reactions to be reversible, but, under certain conditions the reaction will be more likely to go in one direction than the other i.e. it will be spontaneous in one direction but not the other. Factors affecting feasibility are the enthalpy change, the temperature and the ENTROPY change involved in the reaction.

Entropy

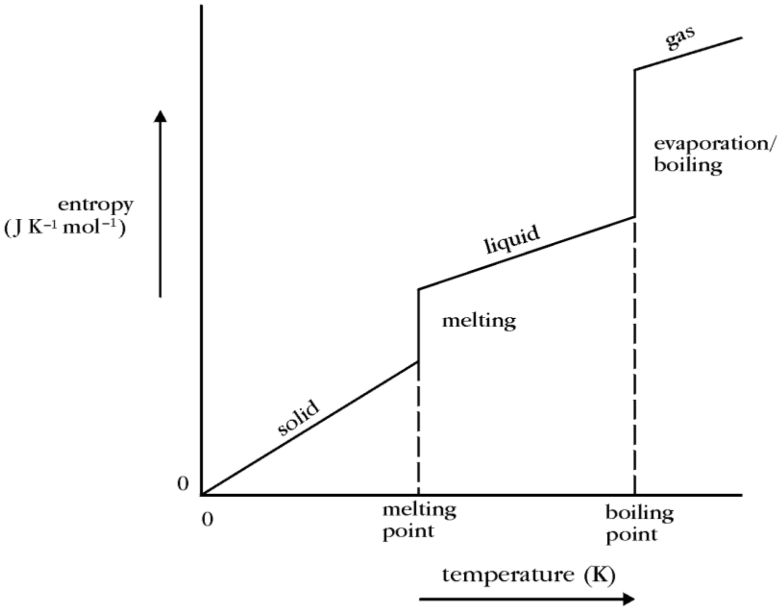
In nature there is a tendency towards disorder. A brick wall changes into a disordered heap of bricks either with age or the demolition squad, but the reverse process does not take place spontaneously, i.e. without outside help. More widely, an untended garden, diffusion, corrosion and the dispersion of sewage into the sea are all examples of systems naturally tending towards disorder. In thermodynamic terms disorder is called entropy. The degree of disorder in a system is called the entropy of that system. The greater the disorder, the greater the entropy.



	Molecular Motion		
	Translation	Rotation	Vibration
Kinetic Energy - Solid	no freedom to move	no freedom to rotate	free to vibrate
Kinetic Energy - Liquid	restricted freedom to move	some freedom to rotate	free to vibrate
Kinetic Energy - Gas	total freedom to move	total freedom to rotate	free to vibrate

The molecular motion of any substance depends on its state. Solids only have vibrational motion while gases have vibration, rotation and translational motion.

It therefore follows that entropy increases as temperature increases and that changes in state, such as melting and evaporation, involve large changes in entropy. When a state change occurs there is a change in entropy without a change in temperature and this is linked to the concept of latent heat (see diagram).



The Second Law of Thermodynamics states that the total entropy of a reaction system and its surroundings always increases for a spontaneous process. A spontaneous process is a process that is thermodynamically possible and this means that it can take place on its own irrespective of how long this requires. It should now become clearer why spontaneous endothermic processes take place. Consider the following endothermic reactions:

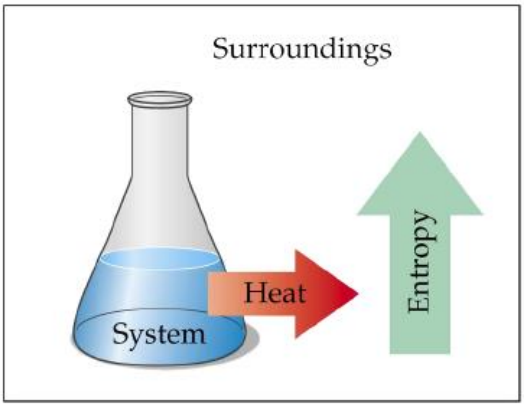
$$CoCl_2.6H_2O(s) + 6SOCl_2(l) \rightarrow CoCl_2(s) + 12HCl(g) + 6SO_2(g)$$

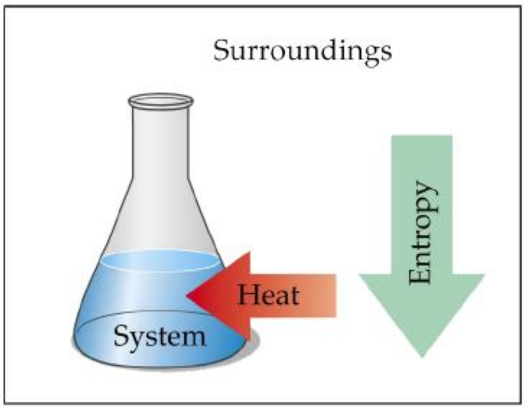
$$Ba(OH)_2.8H_2O(s) + 2NH_4CNS(s) \rightarrow Ba(CNS)_2(aq) + 2NH_3(g) + 8H_2O(l)$$

$$(NH_4)_2CO_3(s) + 2C_2H_5COOH(l) \rightarrow 2NH_4^+C_2H_5COO^-(aq) + H_2O(l) + CO_2(g)$$

It is clear that the entropy of the system increases just by looking at the changes in state from reactants to products. Gases have higher entropy than liquids, which have higher

entropy than solids. This is the basis for the **Third Law of Thermodynamics:** at absolute zero (0 K) a crystal lattice has perfect order and therefore zero entropy.
The entropy increase is so large that it more than counter balances any unfavourable enthalpy changes and the reactions are spontaneous.





We can see that the second law requires that both system and surroundings be taken into account. Heat energy released by a reaction into the surroundings increases the entropy of the surroundings while heat absorbed by a reaction system from the surroundings decreases the entropy of the surroundings.

	Entropy change		
Process	**System**	**Surroundings**	**Overall**
Mixing/expansion	Increase	No change	Increase
Crystallisation	Decrease	Increase	Increase
Polymerisation	Decrease	Increase	Increase
Evolution of life	Decrease	Increase	Increase
Combustion of fuels	Increase	Increase	Increase

The standard entropy of a substance is the entropy for that substance in its standard state and is given the symbol $S°$ (standard conditions are one mole of a substance at one atmosphere pressure and any specified temperature in Kelvin). These values can be used to calculate the standard entropy change for a reaction given that:

$$\Delta S° = \Sigma S° \text{ products} - \Sigma S° \text{ reactants}$$

The unit of entropy change is joules per Kelvin ($J\ K^{-1}$) or joules per Kelvin per mole ($J\ K^{-1}\ mol^{-1}$).

Free energy

We have now established that, in a thermodynamically feasible endothermic reaction, there is a favourable entropy change **inside** the reaction mixture. An endothermic reaction can only take place if its entropy change is sufficiently favourable to 'overcome' the unfavourable enthalpy change. The combination of enthalpy and entropy changes is known as the **free energy change** and is given the symbol ΔG:

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

The sign of the free energy change obtained can be used to predict the possibility of the reaction proceeding. This can be summarised by saying that a **negative** value for the change in free energy shows that the reaction is likely to happen spontaneously. On the other hand, a positive value for ΔG shows that the reaction is unlikely to happen unless external energy is available to do work on the system (e.g. the reaction is heated).

If the values for the enthalpy and entropy changes are known for a reaction, it is possible to calculate the value of the free energy change at any temperature.

If the measurements are all made under standard conditions, then:

$$\boxed{\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}}$$

Although a negative ΔG or ΔG° value allows one to predict that the reaction is feasible, i.e. the reaction will go in the direction of the products, it does not imply anything about the rate of the reaction. The activation energy for the reaction has to be overcome for the reaction to occur and this could be very high and so the reaction could be very slow.

For example, if hydrogen and oxygen gases are mixed, the standard free energy change for the formation of1 mole of water at 298 K is about –237 kJ mol^{-1}. However, virtually no reaction occurs until energy is supplied to overcome the activation energy or a suitable catalyst is added.

The standard free energy change for a reaction can be calculated from tabulated data of standard enthalpy and standard entropy changes for that reaction. In the same way as standard enthalpies of formation can be used to calculate the standard enthalpy change for a reaction, the standard free energy for a reaction can be calculated from the standard free energies of formation:

e.g.

$$\begin{array}{lcc} & 2NO_2 \quad \rightleftharpoons & N_2O_4 \\ \Delta G^\circ_f & 2 \times (+52) & (+98) \end{array}$$

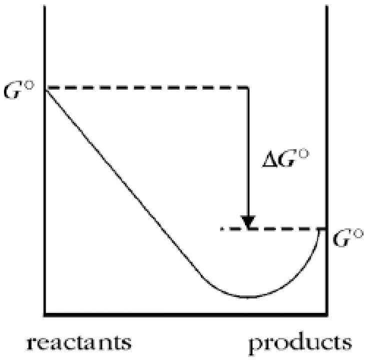
$$\begin{aligned} \text{At 298 K, } \Delta G^\circ &= +98 - (2 \times 52) \\ &= -6 \text{ kJ mol}^{-1} \end{aligned}$$

Free energy and equilibrium

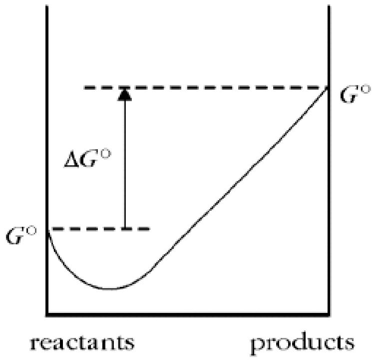
Only when the free energy of the reactants has fallen (by the reactants being used up) to the same value as the products (i.e. ΔG = 0) do we reach equilibrium. At equilibrium, the free energy of the system has reached its minimum value under the given conditions.

In any chemical system once the reaction has started G will be lower than G° since:

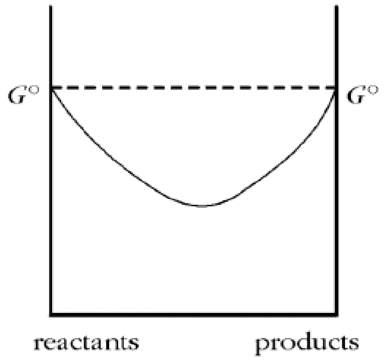
- there is a change from standard conditions
- there is an increased entropy due to the mixing of reactant and product.



ΔG° large and –ve; equilibrium lies on side of products

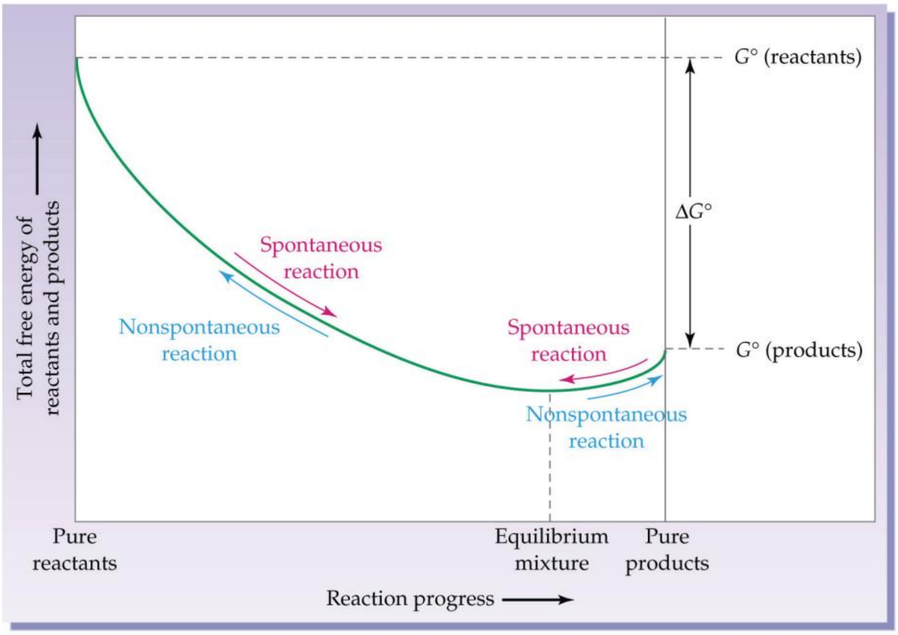


ΔG° large and +ve; equilibrium lies on side of reactants



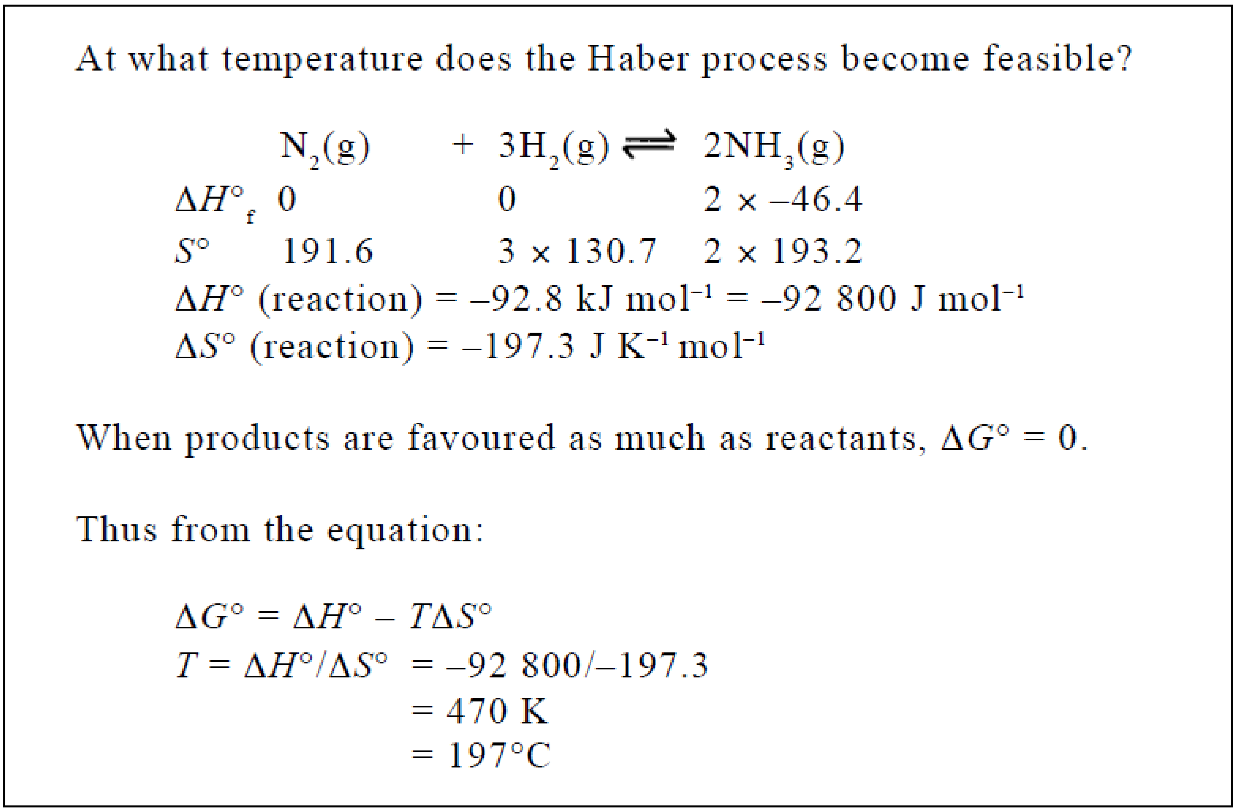
ΔG° is zero; reactants and products equally favoured

The minimum point of the free energy curve corresponds to the position of equilibrium and at this point ΔG = 0.



We can now provide a picture of the difference between ΔG° (standard free energy change) and ΔG. The value of ΔG° tells the observer (outside the reaction) whether the equilibrium position will favour reactants or products. When equilibrium is established, the concentrations of the various species will not be of unit concentration and therefore standard conditions are not applicable. When equilibrium has been established, the ΔG value (inside the reaction) will be zero. Thus, at equilibrium, the free energy of reactants will be equal to the free energy of products and this is why there is no further change in the composition of the reaction with time.

When ΔG° = 0, neither products nor reactants are favoured. This is called the balance point, i.e. products and reactants are equally favoured. It is often possible to calculate the conditions at which the ΔG° value changes from being positive to being negative (which is when ΔG° = 0). This is done by considering only the standard free energies of the reactants and products. This can inform the observer about the conditions at which a reaction is just becoming feasible, i.e. when products are just slightly more favoured than reactants. E.g.



At what temperature does the Haber process become feasible?

	$N_2(g)$	$+\ 3H_2(g) \rightleftharpoons$	$2NH_3(g)$
ΔH°_f	0	0	2 × –46.4
S°	191.6	3 × 130.7	2 × 193.2

ΔH° (reaction) = –92.8 kJ mol^{-1} = –92 800 J mol^{-1}

ΔS° (reaction) = –197.3 J K^{-1} mol^{-1}

When products are favoured as much as reactants, $\Delta G^\circ = 0$.

Thus from the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\begin{aligned} T = \Delta H^\circ/\Delta S^\circ &= -92\ 800/-197.3 \\ &= 470\ \text{K} \\ &= 197^\circ\text{C} \end{aligned}$$

This result can be interpreted as meaning that at 470 K, the reactants and products are equally favoured. By considering the sign of ΔS°, we can work out whether the reaction is feasible at a temperature higher or lower than
470 K. Since ΔS° is negative, –TΔS° is positive. At low temperatures, ΔH° will dominate and ΔG° will be negative. Hence, the Haber process becomes feasible at temperatures below 470 K. By calculating ΔG° at temperatures slightly above and below 470 K, it is possible to see that ΔG° is positive at temperatures above 470 K and negative at temperatures below 470 K.

Therefore, ammonia production is feasible at
temperatures below 470 K. Unfortunately, the industrial reaction cannot be carried out at such a low temperature as a suitable catalyst has not yet been found. It is interesting to note that leguminous plants can bring about this reaction. Current research is trying to identify the enzymes responsible to see if they could be used on an industrial scale.

The calculation does not say anything about either the reaction pathway or the reaction rate. Thermodynamics tells us only how far a reaction will proceed (given enough time), it can never tell us how fast a reaction will take place or by which route. The fact that the standard free energy change is greater than zero does not mean that no reaction takes place. It means that the products are less favoured than the reactants. In industry, equilibrium is rarely allowed to occur. Removal of a product can make a reaction with an unfavourable equilibrium position move in the desired direction.

Questions

1. Calculate the temperature at which the decomposition of barium carbonate becomes feasible.

ΔH° = 268 kJ mol^{-1} ΔS° = 168 J K^{-1} mol^{-1}

Is decomposition more favourable above or below this temperature?

2. The reaction of carbon with steam to produce carbon monoxide and hydrogen is endothermic (ΔH° = 131 kJ mol–1). The reaction is successful at 1500 K when ΔG° = – 71.5 kJ mol^{-1}

(a) Calculate the entropy change for the above reaction at 1500 K.

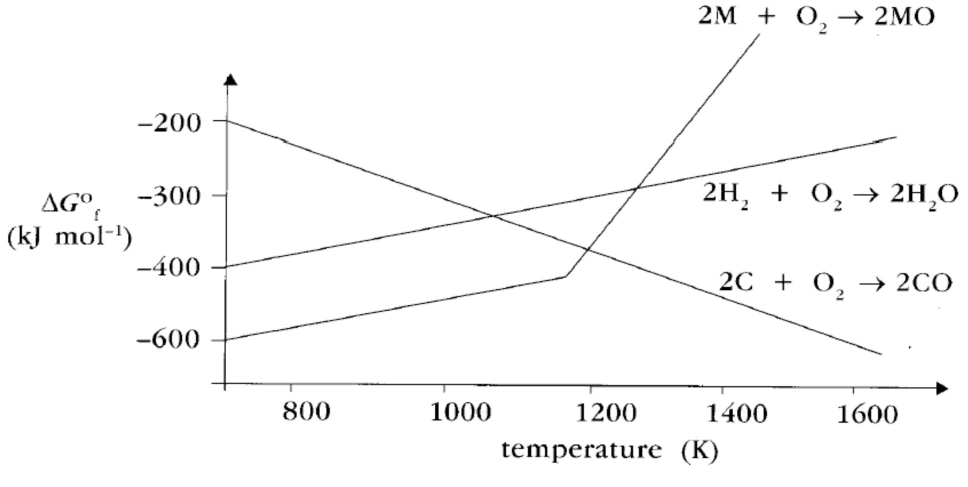
(b) Is the reaction feasible at 25°C?

(c) At which temperature does the reaction just become feasible?

3 .Problem Solving…

Ellingham Diagrams are used to predict whether it is feasible to extract metals from their ores and which reducing agents may be suitable. The following Ellingham diagram shows the dependence of ΔG° on temperature for a range of oxidation reactions:

3.



What is the minimum temperature at which the metal oxide, MO, can be reduced by:

(a) hydrogen
(b) carbon?

Kinetics

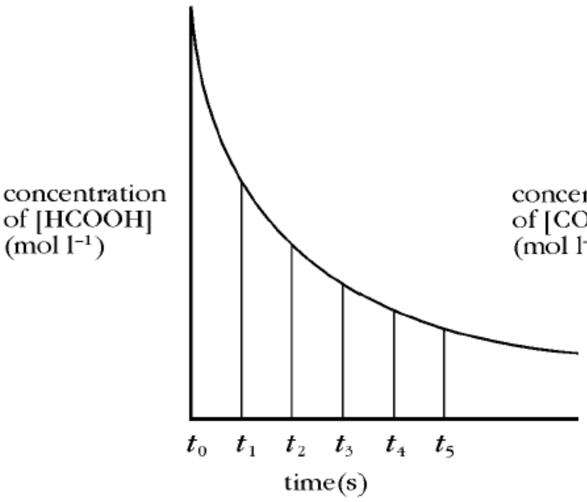
Chemical kinetics is the study of the speed of chemical reactions. From Higher Chemistry it is already known that the speed or rate of a chemical reaction depends on factors such as temperature, concentration of the reactants, particle size and whether a catalyst is present or not. It is also known that all reactions have an activation energy and that an activated complex is formed.

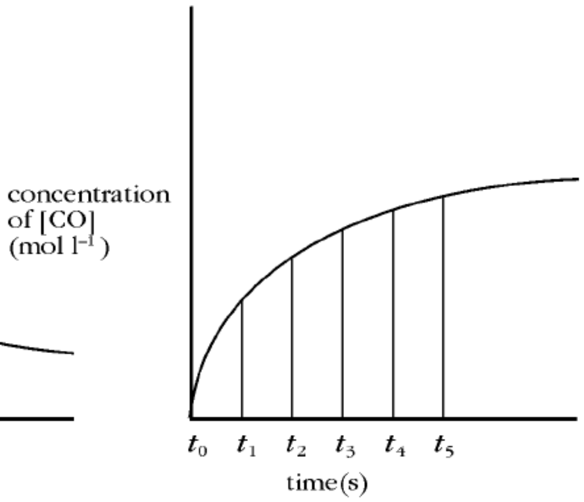
In this section, we are now concerned with the development of these ideas on a more quantitative basis, in which mathematical models are used to state precisely how the concentration of reactants influences the speed of a chemical reaction. We are also interested in how such information can be used to gain an insight into the pathway by which the reaction takes place.
It is customary when dealing with reaction rates to express the rate as a change in concentration of reactant or product in unit time. Expressed in this way, the rate is independent of the size of the sample under consideration.

For example, in the decomposition of methanoic acid:

$HCOOH \rightarrow CO + H_2O$

We can determine the reaction rate by following either the decrease in concentration of the acid or the increase in carbon monoxide concentration with time:





The average reaction rate is the change in concentration of either reactants or products divided by the elapsed time. For example, over the time interval t_1 to t_2:

$$\text{average reaction rate} = \frac{([\text{HCOOH}]_2 - [\text{HCOOH}]_1)}{(t_2 - t_1)}$$

or

$$\text{average reaction rate} = \frac{+([\text{CO}]_2 - [\text{CO}]_1)}{(t_2 - t_1)}$$

(Note that the negative sign is used if we are dealing with reactant concentrations since their concentrations decrease with time.)

It should be clear from the graphs above that, as is the case with most reactions, the rate decreases as the reaction proceeds.

We need to make the elapsed time interval as short as possible, and in effect measure the instantaneous rate, i.e. as Δt approaches zero. We can write, for a very small time interval, d*t*, that the instantaneous rate is:

$$\frac{-\,\mathrm{d}[\mathrm{HCOOH}]}{\mathrm{d}t} \quad \text{or} \quad \frac{+\,\mathrm{d}[\mathrm{CO}]}{\mathrm{d}t}$$

Thus, the rate, at any particular time *t*, is given by the gradient of the tangent to the curve at time *t*. This will have a maximum value at time *t* = 0 and it is therefore usual to determine initial rates of reaction and to use these values in the determination of other kinetic parameters.

Reaction rates and concentration

The qualitative dependence of reaction rate on concentration can be readily demonstrated using a large number of reactions, e.g. the iodine clock reaction, or by measuring the volume of hydrogen produced when magnesium reacts with different concentrations of dilute hydrochloric acid.

If we consider a very simple reaction:

$$\mathrm{A} + \mathrm{B} \rightarrow \text{products}$$

the rate of the forward reaction at any time depends on the concentration of A and B at that time and can be expressed as follows:

$$\text{rate} \propto [\mathrm{A}][\mathrm{B}]$$

$$\text{or} \quad \text{rate} = k[\mathrm{A}][\mathrm{B}]$$

where *k* is the rate constant.

In more general terms, for a simple reaction:

$$nA + mB \rightarrow \text{products}$$

$$\text{rate} = k[A]^n[B]^m$$

This equation is the **rate law.**

The quantities *n* and *m* are termed the orders with respect to the reactants A and B respectively. The overall order of reaction is given as the sum of the powers of the concentration terms that occur in the rate equation, i.e. in the above example the overall order is $n + m$. In simple reactions, the rate law, sometimes called the rate equation, can take one of the forms shown in the table:

Rate law	Order of reaction
rate α $[A]^0$	0
rate α $[A]^1$	1
rate α $[A]^2$	2
rate α $[A]^1[B]^1$	2
rate α $[A]^1[B]^2$	3

These small integral values for the order of reaction are readily understandable if we realise that they refer to the actual number of particles involved in the single step of the reaction that controls the overall reaction rate, i.e. the rate-determining step. This is not necessarily the number of particles involved in the stoichiometric equation. For example, consider the reaction of hydrogen peroxide with hydrogen iodide:

$$H_2O_2 + 2HI \rightarrow H_2O + I_2$$

The experimentally observed rate law is:

$$\text{rate } \alpha[H_2O_2][HI]$$

and consequently the order of reaction is two, whereas the balanced equation has three reactant molecules. The order of reaction is entirely an experimental quantity that is determined solely by finding the rate equation that best fits the experimental data. It cannot be deduced from an examination of the chemical equation for the reaction.

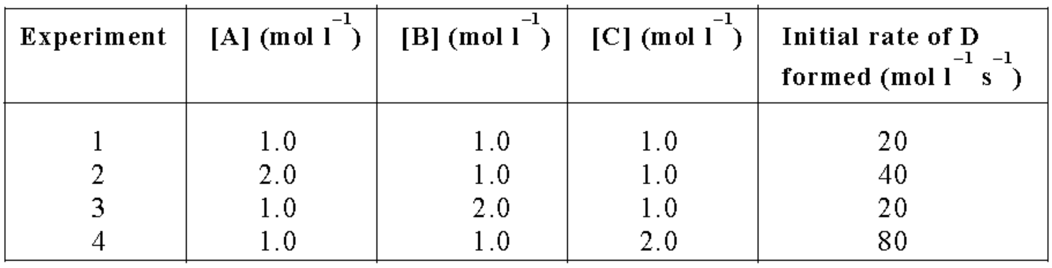
Determining rate constants and orders of reaction

The rate constant of a reaction can be determined from a series of experiments in which the initial concentrations of the reactants are changed. The initial rate of each reaction is calculated and comparisons made:

e.g Consider the following data for an imaginary reaction:

$A + B + C \rightarrow D$

and calculate the rate constant for this reaction.



Experiment	[A] (mol l^{-1})	[B] (mol l^{-1})	[C] (mol l^{-1})	Initial rate of D formed (mol l^{-1} s^{-1})
1	1.0	1.0	1.0	20
2	2.0	1.0	1.0	40
3	1.0	2.0	1.0	20
4	1.0	1.0	2.0	80

From these results we can see that:
(a) doubling [A] doubles the rate (compare 1 and 2)
(b) doubling [B] has no effect on rate (compare 1 and 3)
(c) doubling [C] increases the rate fourfold (compare 1 and 4).

Relating the effect of change in concentration of reactants to the rate ofreaction, the experimental rate law becomes:

rate α $[A][B]^0[C]^2$

or, more simply:

rate α $[A][C]^2$

The reaction is first order with respect to A, second order with respect to C and zero order with respect to B. The overall order is (1 + 2 + 0) = 3.

The rate constant, k, for this reaction is obtained by substituting values from experiment 1 in the rate equation:

rate = $k[A][C]^2$
20 = k[1.0][1.0]
k = 20 $l2\ mol^{-2}\ s^{-2}$

Identical values are obtained using any of the other three sets of results.

Kinetics and reaction mechanism

Chemical kinetics may be thought of as an example of the 'bottle-neck principle', which is frequently observed in everyday life. For instance, a large crowd of people leaving a football ground can only do so at a rate equal to the number who can squeeze through the exit in unit time. It makes no difference whether they run or walk to or from the exit. Similarly, if a chemical reaction proceeds in a series of sequential stages, the overall rate of reaction will be determined by the slowest step, which we call the rate-determining step. The kinetic parameters, which are determined experimentally, refer to this rate-determining step. By reversing the argument, experimentally determined rate equations and orders of reaction can give information about the way in which the reaction occurs. The following three reactions illustrate this.

1. $H_2O_2 + 2HI \rightarrow 2H_2O + I_2$

Experimentally the rate equation is of the form:

rate = $k[H_2O_2][HI]$

This tells us that the rate must be controlled by a step in which one molecule of hydrogen peroxide reacts with one molecule of hydrogen iodide. We can suggest that:

$H_2O_2 + HI \rightarrow X$ (slow rate-determining step)
$X + HI \rightarrow$ products (faster step)

where X is an intermediate formed in the reaction. However, the kinetics themselves give us no direct information about either nature of X or about the total number of steps involved. These must be deduced by other means, such as spectroscopy. The generally accepted mechanism for this reaction is:

$H_2O_2 + HI \rightarrow H_2O + HOI$ (slow step)
$HOI + HI \rightarrow H_2O + I_2$ (faster)

where HOI is an intermediate formed with a transient lifetime.

Hydrolysis of halogenoalkanes (see Unit 2)

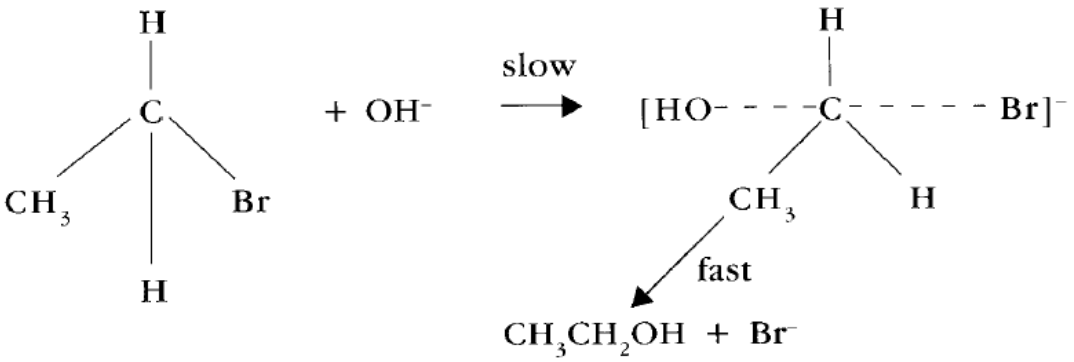
(a) A primary halogenoalkane

$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$

rate = $k[CH_3CH_2Br][OH^-]$

From the rate equation we can deduce that both of the reactants are involved in the rate-determining step. How this takes place is shown below. Itcan be seen that in the slow rate-determining step (in fact the only step in the reaction) the hydroxide ion displaces the bromide ion by attack at the 'back' of the molecule in an SN^2 process (see Unit 2).

3



(b) A tertiary halogenoalkane

$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

The observed rate law depends only on the concentration of the halogenoalkane:

rate = $k[(CH_3)_3CBr]$

The rate-determining step does not, in this case, involve the hydroxide ion. The mechanism can be written as follows:

$(CH_3)_3CBr \rightarrow X^+ + Br^-$ (slow step)
$X^+ + OH^- \rightarrow (CH_3)_3COH$ (faster)

The reaction is a two-step (or, more accurately, more than one-step) process, involving some intermediate (X^+), which by other means we can determine to be the carbocation $(CH_3)_3C^+$.
It has to be emphasised that, on the basis of kinetics alone, we cannot establish the exact mechanism of a reaction. We can only propose a possible mechanism that is consistent with the kinetics.

Questions

The following exothermic reaction takes place in the upper atmosphere where the temperature is much lower than on the Earth's surface.

$$NO + \underset{\text{ozone}}{O_3} \rightarrow NO_2 + O_2$$

In a laboratory- simulated study carried out at room temperature, the following results were recorded.

Relative concentration NO	*Relative concentration* O_3	*Reaction Rate*
1	1	1
2	1	2
1	2	2

a) Write out the rate expression for the reaction.

b) What is the overall order of the reaction ?

c) The reaction in the upper atmosphere is slower than the laboratory reaction for the same relative concentrations of NO and O_3. Account for this observation.

d) From the above equation, comment on the statement “NO catalyses the decomposition of ozone”.

e) In the above reaction, NO removes ozone from the upper atmosphere. Suggest one possible man-made source of oxides of nitrogen which could contribute to this effect

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.
bond enthalpy	For a diatomic molecule XY the molar bond enthalpy is the energy required to break one mole of XY bonds, the products being X and Y. All reactants and products must be in the gas state.
buffer solution	A solution in which the pH remains approximately constant when small amounts of acid or base are added
closed	A closed system has no exchange of matter or energy with its surroundings
complex	A complex consists of a central metal ion surrounded by ligands.
conjugate acid	For every base, there will a conjugate acid formed by gain of a proton (H +)
conjugate base	for every acid, there is a conjugate base formed by loss of a proton (H + ion)
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.

Word	**Meaning**
dynamic equilibrium	A dynamic equilibrium is achieved when the rates of two opposing processes become equal, so that no net change results
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.
end point.	The end point of a titration is the point when the reaction is shown to be complete. This is frequently signalled by the change in colour of an indicator.
enthalpy of neutralisation	The enthalpy change when the acid is neutralised to form one mole of water
enthalpy of solution	The enthalpy change when one mole of a substance is dissolved completely in water
entropy	The entropy of a system is the degree of disorder of the system. The greater the disorder, the greater the entropy. Low entropy is associated with strongly ordered substances
equivalence point	the equivalence point in a titration experiment is reached when the reaction between the titrant (added from the burette) and the titrate (in the flask) is just complete.
First Law of Thermodynamics	states that the total energy of the universe is constant – energy can nether be created nor destroyed
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.

Word	**Meaning**
Hess's Law	Hess's Law states that the overall reaction enthalpy is the sum of the reaction enthalpies of each step of the reaction.
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.
intermediate	A species that is formed in one step of a reaction mechanism and then used up in a subsequent step
Ligands	Molecules or ions that bond to the central metal ion in a complex.
mean molar bond enthalpy	An average value that is quoted for a bond that can occur in different molecular environments
molar bond enthalpy	The molar bond enthalpy for a diatomic molecule X-Y is the energy required to break one mole of X-Y bonds, that is for the process: $X - Y(g)$ $X(g) + Y(g)$
molar solution	A molar solution contains 1 mole of solute in 1 litre of solution.
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.
monoprotic	an acid which is able to produce one H^+ ion from each molecule
order of a reaction	The power to which the concentration of a particular reactant is raised in the rate equation

Word	Meaning
overall order of a reaction	The sum of the powers to which the concentrations of all reactants in the rate equation are raised in the rate equation
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.
quantitative reaction	A quantitative reaction is one in which the reactants react completely according to ratios in the balanced stoichiometric equation.
rate constant	In a rate equation, k is the rate constant and has a constant value for a given reaction at a particular temperature
rate determining step	The slowest step in a reaction mechanism that governs the overall rate
rate equation	An equation that tells how the reaction rate depends on the concentration of each reactant
reaction mechanism	The series of simple steps by which a chemical reaction occurs
reduction	This is the gain of electrons by a substance. It can also be described as a decrease in oxidation number.
Second Law of Thermodynamics	The total entropy of a reaction system and its surroundings always increases for a spontaneous change
spectrochemical series	A list of ligands in order of the size of the crystal field splitting caused in the d orbitals.
stable equilibrium	A stable equilibrium state is one which is regained after a small disturbance from this state occurs.

Word	Meaning
standard conditions	Conditions at a pressure of one atmosphere and a specific temperature (298 K)(25°C).
standard enthalpy change	The enthalpy change for a reaction in which reactants and products are considered to be in their standard states at a specified temperature
standard Gibbs free energy	The standard Gibbs free energy change for a reaction is related to the standard enthalpy and entropy changes by $\Delta G° = \Delta H° - T\Delta S°$ The direction of spontaneous change is in the direction of decreasing free energy.
standard molar enthalpy of combustion	The enthalpy change when one mole of a substance is completely burned in oxygen under standard conditions.
standard molar enthalpy of formation	The enthalpy change that occurs when one mole of a substance is produced from its elements in their standard states
standard solution	A standard solution is one with an accurately known concentration. It can be prepared by weighing a primary standard and dissolving it in a known volume of solution, or by titrating against another standard solution.
standard state	The most stable state of a substance or element under standard conditions
Third Law of Thermodynamics	The Third Law of Thermodynamics states that the entropy of a perfect crystal at 0 K is zero
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 cm^{-1} (number of cycles per cm.)