Chapter 2

Atomic theory

Our study of atomic theory can be split into two main parts. The first is how we arrive at a general model of an atom and study the properties of atoms such as their masses and structure; the second is the detailed electron configuration of atoms.

2.1 The atom

We should be able to complete the classic table for the sub-atomic particles:

	Relative mass	Relative charge	Location
Proton			
		0	
	$\frac{1}{1840}$		

We should be able to recognise and define the parts of the general symbol for an element, X: ${}^{A}_{Z}\mathrm{X}$.

The atomic number, Z defines what an element is. It tells us the number of protons in the nucleus of an atom of an element.

The mass number, A is the number of protons and neutrons in the nucleus of an atom of an element.

Isotopes are atoms of the same element with different numbers of neutrons (the same numbers of protons) and therefore different mass numbers. For instance ${}^{35}_{17}\mathrm{Cl}$ and ${}^{37}_{17}\mathrm{Cl}$ Isotopes have identical chemical properties (as their electronic behaviour is the same) but different physical properties. For instance, ${}^{35}_{17}\mathrm{Cl}$ is less dense than ${}^{37}_{17}\mathrm{Cl}$ and ${}^{14}_{6}\mathrm{C}$ is radioactive whereas ${}^{12}_{6}\mathrm{C}$ isn't. You can use your knowledge of isotopes to calculate and explain non-integer relative atomic masses. The classic example is chlorine, which has a relative atomic mass of 35.5 because 75% of Cl atoms are ${}^{35}_{17}\mathrm{Cl}$

and the other 25% are ${}^{37}_{17}\mathrm{Cl}$. The weighted average of the masses is:

$$\frac{(35 \times 75) + (37 \times 25)}{100} = 35.5$$

You should be able to calculate the numbers of protons, neutrons and electrons in an atom *or ion* given the symbol, A and Z. For instance, how many protons, neutrons and electrons are there in the following?

	${}^{27}_{13}\mathrm{Al}$	${}^{56}_{26}\mathrm{Fe}^{2+}$	${}^{23}_{11}\mathrm{Na}^{+}$
Protons			
Neutrons			
Electrons			

2.1.1 The Mass Spectrometer

You need to be able to memorise the diagram of the mass spectrometer as given in a text book (Green & Damji (p65) and Geoff (p6) are both good) and you should be able to explain the functions of the parts.

- **Vaporisation** The sample is turned into vapour and injected into the instrument
- **Ionisation** Neutral atoms or molecules are converted into (normally unipositive) ions by bombardment by fast-moving electrons which are emitted from a heated cathode (they accelerate toward a positive plate). These electrons hit electrons in the particle and knock them off. It's a bit like ionisation, $\mathrm{X}_{(g)} + e^{-} \longrightarrow \mathrm{X}^{+}_{(g)} + 2e^{-}$, although not exactly the same.
- **Acceleration** The positive ions are accelerated through an electric field. The ions are also passed through slits / holes in parallel plates which serve to create a 'beam' of ions.
- **Deflection** The fast-moving positive ions are deflected by a magnetic field which is generated by an electromagnet. Heavier ions are deflected less. Ions with lower charges are deflected less, although we normally only meet ions with a single charge.
- **Detection** The strength of the magnetic field can be controlled, as it is an electromagnet. Varying the strength enables ions of different masses to be deflected the right amount to hit the detector. Hence the abundance (relative amounts) of ions with a particular mass/charge ratio is determined, although as

the charge is normally 1 we see the relative abundances of ions with particular masses.

Mass spectra can be used to determine relative atomic masses. For instance, the mass spectrum of chlorine atoms would show two peaks. One would be at mass/charge = 35 and the other at 37. The more abundant peak is always scaled up to 100, which would be the peak at 35; the other peak would have height 33. The relative atomic mass is given by

$$\frac{(35 \times 100) + (37 \times 33)}{(100 + 33)} = 35.5$$

which is reassuringly the answer we were expecting. Other examples are given in Green & Damji (p66).

2.2 Atomic Structure

The detailed structure of atoms which is of interest to chemists is the electron arrangement. To understand the evidence we have about electronic structure we need to understand the nature of energy and light.

2.2.1 The electromagnetic spectrum

The electromagnetic spectrum shows us the relationship between the frequency and wavelength of radiation. The electromagnetic spectrum ranges from gamma rays to radio waves, with visible light somewhere in between. All these types of radiation travel at the speed of light. Radio waves have long wavelengths and low frequencies. Gamma rays have short wavelengths and high frequencies. The relationship between speed, wavelength and frequency is given by

$$c = f\lambda \tag{2.1}$$

in which c is the speed of light, and is approximately equal to 3×10^8 m s^{-1}. The energy of radiation is directly proportional to its frequency - higher frequency means higher energy.

$$E = h\ f \tag{2.2}$$

in which h is Planck's constant, with value 6.63×10^{-34}J s. All of this means that radio waves are far less energetic than gamma rays, which is why radios are a lot safer than nuclear weapons.

2.2.2 Light spectra

A normal light bulb will emit white light, which comprises all the colours of light. If we passed the light from a regular bulb through a prism we would get a *continuous spectrum* showing all the colours of the rainbow. Ahhhh. Where does this light come from?

The filament in a light bulb has electricity passed through it. When enough energy is given to the filament it heats up (simple resistance). More current makes it heat up so much that it emits light. The electrons in the wire get given some energy and are *excited*. There is no reason that they can not return to their previous *ground state* and when they do this they must lose some energy. The frequency of the energy emitted depends on how big the energy gap between the excited and ground state is. If this frequency is in the visible spectrum we can actually see the radiation emitted. Lots of different possible energy gaps exist in regular light bulbs, so lots of colours are produced, and we see the overall effect as white light. Light bulbs get hot because they also emit a lot of energy in the infra red region of the spectrum (this makes them relatively inefficient, as the heat emitted is not used for anything).

2.2.3 Atomic spectra

Some bulbs don't produce white light. Sodium lamps, such as those used in street lighting, produce a yellow / orange light. When this light is shone through a prism only a particular colour comes out. This is an example of a *line spectrum*. The light is produced in the same way as in a regular bulb - excited electrons lose energy and the frequency of the energy corresponds to the gap between the excited and ground states. In the case of the sodium lamp however there are not lots of transitions which happen - the only one in the visible spectrum corresponds to yellow / orange light and so we only see this one colour.

In fact all elements have their own characteristic line spectra, although not all of them would produce colours in the visible spectrum. We saw this in the flame test practical - certain elements produce certain colours of light. The element normally used in light bulbs is tungsten - this is a heavy atom with a very high melting point - the line spectrum is actually continuous in the visible region, and only shows discrete lines in the ultra violet. If we look at the line spectra of elements (not just in the visible) we will see that the lines start to converge at higher frequencies (towards the ultra violet). You can find pictures of atomic spectra here:

`http://library.thinkquest.org/19662/images/eng/pages/model-bohr-3.jpg`

`http://www.cbu.edu/ jvarrian/252/emspex.jpg`

2.2.4 The hydrogen emission spectrum

The hydrogen atom only contains one electron and one proton. This simplicity means that hydrogen atoms have the simplest atomic spectra. You should be able to sketch energy level diagrams such as those shown in your text books, with a large gap between $n = 1$ and $n = 2$, a smaller gap between $n = 2$ and $n = 3$ and so on. The energy levels should converge as $n \to \infty$.

The hydrogen emission spectrum contains 6 series of lines, all of which show convergence. You need to know the Lyman series in the ultra violet (which contains the largest energy change, from higher n to $n = 1$), the Balmer series in the visible ($\to n = 2$), and the Paschen series in the infra red ($\to n = 3$). Note that the Lyman series contains the largest energy transitions as it includes the largest gap between energy levels.

The electron in a hydrogen atom can only occupy particular energy levels which are labelled with the principal quantum number n. The energy levels are also called shells. $n = 1$ is the ground state of the electron, but note that even though this is the lowest energy level the electron can occupy it does not have zero energy. When the hydrogen atom is excited by absorbing energy the electron can jump up to a higher energy level. This excited atom can then emit energy in the form of electromagnetic radiation if the electron falls down to a lower energy level. The frequency of the energy emitted corresponds directly to the size of the energy gap between the excited and lower level, as given by equation 2.2. A line is seen in the emission spectrum of the element. These lines are excellent evidence for the *quantisation* of electron energy levels in atoms. If the energies weren't quantized the emission spectrum of hydrogen would be continuous.

It is significant that the energy levels converge. If an electron is excited to $n = \infty$ it falls off the atom - the atom is ionised. This process can be represented by the equation:

$$\mathrm{X}_{\,(\mathrm{g})} \longrightarrow \mathrm{X}^{+}_{(\mathrm{g})} + \mathrm{e}^{-} \tag{2.3}$$

This energy can be determined for the hydrogen atom. The Lyman series is the highest energy group of transitions in hydrogen, they are transitions to $n = 1$. The ionisation energy is the transition $n = 1 \longrightarrow n = \infty$. The energy at which the Lyman series converges (the lines get closer and closer and closer together) is the ionisation energy. There are no lines in the hydrogen emission spectrum at a higher energy.

Remember that these emission spectra are the results of transitions of electrons in millions of atoms - all possible electronic transitions occur lots and lots of times. This is why we see all the possible transitions clearly.

2.2.5 Atomic orbitals

The main energy levels are split into subshells. The number of subshells is given by the number of the energy level, so $n = 3$ has 3 subshells. The sublevels are labelled s, p, d and f. s can hold 2 electrons, p can hold 6, d can hold 10 and f can hold 14.

Electrons can have particular energies, and these are shown by the energy levels. However, electrons exist and need to occupy some space. The spaces where electrons exist in atoms are called *orbitals*. An orbital defines the region in space where an electron is likely to be found.

- Each orbital can hold a maximum of two electrons
- The first four types of orbital (and the only ones you're ever likely to need to know about) are labelled s, p, d and f
- You need to be able to describe and draw an s orbital (it's spherical) and a p orbital (it's dumbell shaped)

$n = 1$	one	subshell	1s	2 electrons
$n = 2$	two	subshells	2s 2p	8 electrons
$n = 3$	three	subshells	3s 3p 3d	18 electrons
$n = 4$	four	subshells	4s 4p 4d 4f	32 electrons

This means that each s sublevel contains 1 s orbital (it can hold 2 electrons), each p sublevel contains 3 p orbitals (it can hold 6 electrons), each d sublevel contains 5 d orbitals (it can hold 10 electrons), each f sublevel contains 7 f orbitals (it can hold 14 electrons). The blocks in the long form of the periodic table are 2, 6, 10 and 14 elements wide, corresponding to s, p, d and f outermost electrons.

2.2.6 Filling of energy levels

In hydrogen the energy levels fill up in a sensible order - 1s, 2s, 2p, 3s, 3p, 3d, 4s etc. Unfortunately this doesn't happen in any other elements. It is found that the 4s level is actually lower in energy than the 3d, so the 4s is filled before the 3d. When electrons are lost however, the 4s electrons are actually easier to remove than the 3d (they are the outermost electrons). This means that transition metals such as iron lose their 4s electrons before they start to lose their 3d electrons.

2.2.7 Electronic configuration

The easy way to describe the electronic configuration of aluminium is the 'GCSE' way: 2, 8, 3. Our knowledge of atomic structure tells us that the real situation is actually more complex than this. The filling of atomic orbitals is governed by some rules:

- **The Aufbau (building up) principle** states that electrons fill atomic orbitals in order of increasing energy
- **The Pauli exclusion principle** states that no more than two electrons can occupy an atomic orbital
- **Hund's rule** states that where orbitals of equal energy are available the orbitals first fill with one electron each with parallel spins before a second is added with a paired (opposite) spin

The upshot of this is that the electronic configuration of aluminium is actually $1s^2 2s^2 2p^6 3s^2 3p^1$. Potassium is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ not $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ because the 4s energy level is lower in energy than the 3d.

2.2.8 Ionisation energies

Ionisation energy is the energy required to remove 1 mole of electrons from one mole of gaseous atoms to produce 1 mole singly charged positive ions in the gas phase, as in equation 2.3. All ionisation energies are positive because we are giving an electron energy to get to $n = \infty$.

You should look at the plots of ionisation energies in your notes and relate them to the rules for filling orbitals given above and be able to explain the little bumps.

The general trend is for ionisation energies to increase across a period and decrease down a group.

Dips seen going from s to p sublevels (for instance, Be to B) can be explained thus: There is a decrease because the electron removed from B is in a p sublevel. This electron is at a higher energy than the s sublevel and is further from the nucleus and therefore easier to remove.

Dips halfway along the p block (for instance going from N to O): There is a decrease because the N has singly filled p orbitals (Hund's rule), whereas the O has one doubly filled p orbital resulting in greater electron-electron repulsion and therefore lower ionisation energy.