1. Atoms

The aim of this chapter is to introduce concepts and theory that is necessary to have knowledge about in order to get a general introduction into the field of chemistry and to get an understanding of many fundamental aspects concerning chemistry. Initially we are going to look at the single atom itself and then we move to the arrangement of the elements into the periodic table.

1.1 Atomic nucleus, electrons and orbitals

The topic of this first chapter is the single atom itself. All matter is composed of atoms and to get a general understanding of the composition of atoms and their nature we first have to learn about electromagnetic radiation. Electromagnetic radiation is closely related to the nature of atoms and especially to the positions and movements of the electrons relative to the atomic nuclei.

1.1.1 Components of the atom

An atom is composed of a *nucleus* surrounded by *electrons*. The nucleus consists of positively charged *protons* and uncharged *neutrons*. The charge of an electron is *-1* and the charge of a proton is *+1*. An atom in its ground state is neutral (uncharged) because is consists of an equal amount of protons and electrons. The number of neutrons in the nucleus of an element can however vary resulting in more than one *isotope*. Hydrogen for example has three isotopes:

$$\left.\begin{array}{l}\text{- Hydrogen, H, Nucleus composition : 1 proton + 0 neutrons}\\ \text{- Deuterium, D, Nucleus composition : 1 proton + 1 neutron}\\ \text{- Tritium, T, Nucleus composition : 1 proton + 2 neutrons}\end{array}\right\}\text{the 3 isotopes of hydrogen}$$

The three isotopes of hydrogen each have its own chemical symbol (H, D and T) whereas isotopes of other elements do not have special chemical symbols. Many elements have many isotopes but only relatively few of these are stable. A stable isoptope will not undergo radioactive decay. The nucleus of an unstable isotope on the other hand will undergo radioactive decay which means that the nucleus will transform into other isotopes or even other elements. In the following example we will look more at isotopes for the element uranium.

Example 1- A:
Two isotopes of uranium

A classical example of an element with unstable isotopes is uranium. Uranium-235 is a uranium isotope in which the nucleus consists of 92 protons and 143 neutrons (92 + 143 = 235). *Nucleons* are a common designation for both protons and neutrons since they are both positioned in the nucleus. Uranium-238 is another uranium isotope in which the nucleus consists of 92 protons and 146 neutrons (total number of nucleons = 92 +146 = 238). These to uranium isotopes can be written as follows:

$$^{235}_{92}U, \quad 92 \;\; protons, \quad total \;\; 235 \;\; nucleons \;\; (235 - 92 = 143 \;\; neutrons)$$

$$^{238}_{92}U, \quad 92 \;\; protons, \quad total \;\; 238 \;\; nucleons \;\; (238 - 92 = 146 \;\; neutrons)$$

It is seen that the two isotopes do not have special chemical symbols. They both use the "U" for *uranium* followed by the number of total amount of nucleons which in this case is 235 and 238 respectively.

The nucleus constitutes only a very small part of the total volume of the atom. If an atom is compared with an orange (100 mm in diameter) the nucleus will be placed in the centre with a diameter of only 0.001 mm.

The weight of a proton and a neutron is approximately the same ($1.67 \cdot 10^{-27}$ kg) whereas the weight of an electron is only 0.05% of this weight ($9.11 \cdot 10^{-31}$ kg). If an atom lets off or receives electrons it becomes an *ion*. An ion is either positively or negatively charged. If an atom lets off one or more electrons the overall charge will becomes positive and you then have a so-called *cation*. If an atom receives one or more electrons the overall charge will be negative and you then have a so-called *anion.*

When electrons are let off or received the *oxidation state* of the atom is changed. We will look more into oxidation states in the following example.

Example 1- B:
Oxidation states for single ions and composite ions

When magnesium and chlorine reacts, the magnesium atom lets of electrons to chlorine and thus the oxidations states are changed:

$$Mg \quad \rightarrow \quad Mg^{2+} \quad + \quad 2e^{-} \qquad Oxidation\ \ state\ \ for\ \ magnesium\ \ ion: \ \ 0 \rightarrow +2$$

$$2\ \ Cl \quad + \quad 2e^{-} \quad \rightarrow \quad 2\ \ Cl^{-} \qquad Oxidation\ \ state\ \ for\ \ chloride: \ \ 0 \rightarrow -1$$

$$Mg \quad + \quad 2\ \ Cl \quad \rightarrow \quad MgCl_2$$

One sees that the oxidation state equals the charge of the ion. The cations are normally named just by adding “ion” after the name of the element (Mg^{+} = magnesium ion) whereas the suffix “-id” replaces the suffix of the element for anions (Cl^{-} = chloride). For composite ions, a shared (total) oxidation number is used. This shared oxidation state is the sum of all the oxidation states for the different ions in the composite ion. Uncharged atoms have the oxidation number of zero. The ammonium ion and hydroxide are both examples of composite ions:

$$NH_4^{\ +} \qquad Oxidation\ \ state\ \ for\ \ ammonium: \ \ +1$$

$$OH^{-} \qquad Oxidation\ \ state\ \ for\ \ hydroxide: \ \ -1$$

The oxidation state for hydride is always ”+1” (H^{+}) and the oxidation state for oxide is always “-2” (O^{2-}). However there are exceptions. For example the oxidation state of oxygen in hydrogen peroxide (H_2O_2) is “-1” and in lithium hydride (LiH) the oxidation state of hydrogen is “-1”.

1.1.2 Electron movement and electromagnetic radiation

Description of the position of the electron relative to the atomic nucleus is closely related to emission or absorption of electromagnetic radiation. Therefore we are going to look a bit more into this topic. Energy can be transported by electromagnetic radiation as waves. The wavelength can vary from 10^{-12} meter (gamma radiation) to 10^4 meter (AM radio waves). Visible light is also electromagnetic radiation with wavelengths varying from $4 \cdot 10^{-7}$ meter (purple light) to $7 \cdot 10^{-7}$ meter (red light). Thus visible light only comprises a very small part of the electromagnetic spectrum.

Light with different wavelengths have different colours. White light consists of light with all wavelengths in the visible spectrum. The relationship between wavelength and frequency is given by the following equation:

$$c = \lambda \cdot f, \quad c = 3 \cdot 10^8 m/s \tag{1- 1}$$

The speed of the light c is a constant whereas λ denotes the wavelength of the light and f denotes the frequency of the light. When light passes through for example a prism or a raindrop it diffracts. How much it diffracts is dependent on the wavelength. The larger the wavelength is, the less is the diffraction and the smaller the wavelength is, the larger is the diffraction. When white light (from the sun for example) is sent through a prism or through a raindrop it thus diffracts into a continuous spectrum which contains all visible colours from red to purple (all rainbow colours) which is sketched in Figure 1- 1.

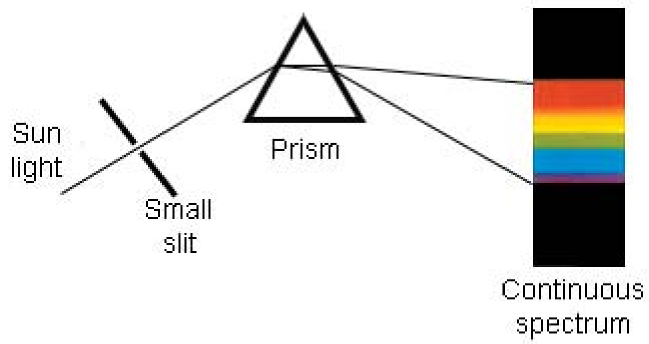

Figure 1- 1: Continuous spectrum.
Diffraction of sun light into a continuous colour spectrum.

When samples of elements are burned off, light is emitted, but this light (in contrast to a continuous spectrum) is diffracted into a so-called *line spectrum* when it passes through a prism. Such an example is sketched in Figure 1- 2.

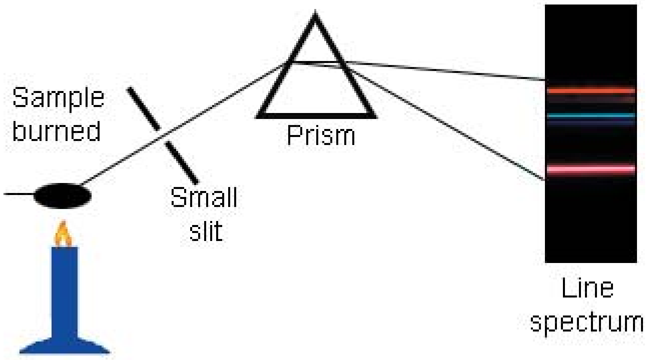

Figure 1- 2: Line spectrum.
Light from the burning off of a sample of an element diffracts into a line spectrum.

Thus only light with certain wavelengths are emitted corresponding to the individual lines in the line spectrum when an element sample is burned off. How can that be when light from the sun diffracts into a continuous spectrum? Many scientists have during the years tried to answer this question. The overall answer is that it has got something to do with the positions of the electrons relative to the atomic nucleus. We will try to give a more detailed answer by explaining different relevant theories and models concerning this phenomenon in the following sections.

1.1.3 Bohr's atomic model

Based on the line spectrum of hydrogen the famous Danish scientist Niels Bohr tried to explain why hydrogen only emits light with certain wavelengths when it is burned off. According to his theory the electrons surrounding the nucleus are only able to move around the nucleus in certain circular orbits. The single orbits correspond to certain energy levels. The orbit closest to the nucleus has the lowest energy level and is allocated with the *primary quantum number* $n = 1$. The next orbit is allocated with the primary quantum number $n = 2$ and so on. When hydrogen is in its *ground state* the electron is located in the inner orbit ($n = 1$). In Figure 1- 3 different situations are sketched. The term "photon" will be explained in the next sub section and for now a photon is just to be consideret as an electromagnetic wave.

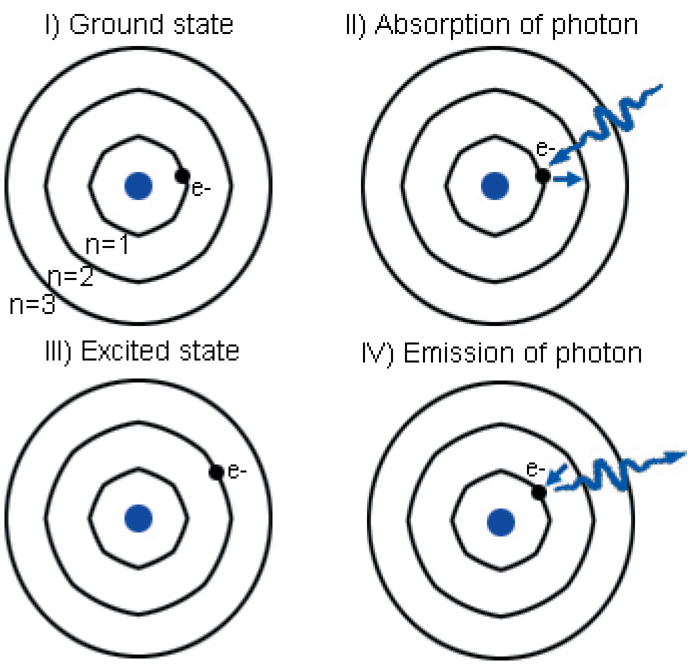

Figure 1- 3: Bohr's atomic model for hydrogen.
Sketch of the hydrogen atom according to Niels Bohr's atomic model. Only the inner three electron orbits are shown. I) The hydrogen atom in its ground state. II) The atom absorbs energy in the form of a photon. The electron is thus supplied with energy so that it can "jump" out in another orbit. III) The hydrogen atom is now in excited state. IV) The electron "jumps" back in the inner orbit. Thus the atom is again in ground state. The excess energy is released as a photon. The energy of the photon corresponds to the energy difference between the two inner orbits in this case.

If the atom is supplied with energy (for example by burning) the electron is able to "jump" out in an outer orbit ($n > 1$). Then the atom is said to be in *excited state*. The excited electron can then "jump" back into the inner orbit ($n = 1$). The excess energy corresponding to the energy difference between the two orbits will then be emitted in the form of electromagnetic radiation with a certain wavelength. This is the answer to why only light with certain wavelengths are emitted when hydrogen is burned off. The different situations are sketched in Figure 1- 3. Bohr's atomic model could explain the lines in the line spectrum of hydrogen, but the model could not be extended to atoms with more than one electron. Thus the model is considered as being fundamentally wrong. This means that other models concerning the description of the electron positions relative to the nucleus are necessary if the line spectra are to be explained and understood. We are going to look more into such models in the sections *1.1.6 Wave functions and orbitals* and *1.1.7 Orbital configuration*, but first we have to look more at photons.

1.1.4 Photons

In section *1.1.2 Electron movement and electromagnetic radiation* electromagnetic radiation is described as continuous waves for which the connection between wavelength and frequency is given by equation (1- 1) on page 15. With this opinion of electromagnetic radiation, energy portions of arbitrary size are able to be transported by electromagnetic radiation. The German physicist Max Planck disproved this statement by doing different experiments. He showed that energy is *quantized* which means that energy *only* can be transported in portions with specific amounts of energy called *quantums*. Albert Einstein further developed the theory of Planck and stated that *all* electromagnetic radiation is quantized. This means that electromagnetic radiation can be considered as a stream of very small "particles" in motion called *photons*. The energy of a photon is given by equation (1- 2) in which h is the Planck's constant and c is the speed of the light.

$$E_{photon} = h \cdot \frac{c}{\lambda}, \quad h = 6.626 \cdot 10^{-34}\, J \cdot s, \quad c = 3 \cdot 10^{8}\, m/s \tag{1- 2}$$

It is seen that the smaller the wavelength is, the larger is the energy of the photon. A photon is not a particle in a conventional sense since it has no mass when it is at rest. Einstein revolutionized the physics by postulating a connection between mass and energy. These two terms were previously considered as being *totally* independent. On the basis of viewing electromagnetic radiation as a stream of photons, Einstein stated that energy is actually a form of mass and that all mass exhibits both particle and wave characteristics. Very small masses (like photons) exhibit a little bit of particle characteristics but predominantly wave characteristics. On the other hand, large masses (like a thrown ball) exhibit a little bit of wave characteristics but predominantly particle characteristics. These considerations results in this very famous equation:

$$E = m \cdot c^2, \quad c = 3 \cdot 10^{8}\, m/s \tag{1- 3}$$

The energy is denoted E and hence the connestion postulated by Einstein between energy and mass is seen in this equation. The previous consideration of electromagnetic radiation as continuous waves being able to transport energy with no connection to the term "mass" *can* however still find great applications since photons (as mentioned earlier) mostly exhibit wave characteristics and only to a very little extent particle (mass) characteristics. In the following example we will se how we can calculate the energy of a photon by use of some of the presented equation from this sub section.

Example 1- C:
Energy of a photon

A lamp emits blue light with a frequency of $6.7{\cdot}10^{14}$ Hz. The energy of one photon in the blue light is to be calculated. Since the frequency of the light is known, equation (1- 1) on page 15 can be used to calculate the wavelength of the blue light:

$$c = \lambda \cdot f \Leftrightarrow \lambda = \frac{c}{f} = \frac{3 \cdot 10^{8}\ m/s}{6.7 \cdot 10^{14}\ s^{-1}} = 4.5 \cdot 10^{-7}\, m$$

This wavelength of the blue light is inserted into equation (1- 2) (from page 18):

$$E_{photon} = h \cdot \frac{c}{\lambda} = 6.626 \cdot 10^{-34}\, J \cdot s \cdot \frac{3 \cdot 10^{8}\, m/s}{4.5 \cdot 10^{-7}\, m} = 4.4 \cdot 10^{-19}\, J$$

Now we have actually calculated the energy of one of the photons in the blue light that is emitted by the lamp. From equation (1- 2) it is seen that the smaller the wavelength is, the more energy is contained in the light since the photons each carries more energy.

In the next example we are going to use the famous Einstein equation (equation (1- 3) on page 18) to evaluate the stability of a tin nucleus.

Example 1- D:
Mass and energy (Einstein equation)

From a thermodynamic point of view the stability of an atomic nucleus means that in terms of energy it is favourable for the nucleus to exist as a whole nucleus rather than split into two parts or (hypothetically thinking) exist as individual neutrons and protons. The thermodynamic stability of a nucleus can be calculated as the change in potential energy when individual neutrons and protons join and form a nucleus. As an example we are going to look at the tin isotope tin-118. Tin is element number 50 and thus this isotope contains 50 protons and 118 – 50 = 68 neutrons in the nucleus. In order to calculate the change in energy when the nucleus is "formed" we first have to determine the change in mass when the following hypothetic reaction occurs:

$$50\ {}^{1}_{1}p \quad + \quad 68\ {}^{1}_{0}n \quad \rightarrow \quad {}^{118}_{50}Sn$$

The mass on the right side of this reaction is actually not the same at the mass on the left side. First we will look at the masses and change in mass:

Mass on left side of the reaction:

$$Mass\left(50{}^{1}_{1}p + 68{}^{1}_{0}n\right) = 50 \cdot 1.67262 \cdot 10^{-27}\,kg + 68 \cdot 1.67497 \cdot 10^{-27}\,kg = 1.97526 \cdot 10^{-25}\,kg$$

Mass on right side of the reaction:

$$Mass\left({}^{118}_{50}Sn\right) = \frac{117.90160 \cdot 10^{-3}\,kg/mol}{6.022 \cdot 10^{23}\,mol^{-1}} = 1.95785 \cdot 10^{-25}\,kg$$

Change in mass when reaction occurs (tin-118 formation):

$$Mass\ \ change = 1.95785 \cdot 10^{-25}\,kg - 1.95785 \cdot 10^{-25}\,kg = -1.74145 \cdot 10^{-27}\,kg$$

It is thus seen that when the reaction occurs and the tin-118 nucleus is formed, mass "disappears". This change in mass can be inserted into the famous Einstein equation (equation (1- 3) on page 18) and the change in potential energy can be calculated.

$$\Delta E = \Delta m \cdot c^2 \Leftrightarrow$$
$$\Delta E = -1.74145 \cdot 10^{-27}\,kg \cdot \left(3 \cdot 10^{8}\,m/s\right)^2 = -1.6 \cdot 10^{-10}\,J$$

It is seen that the "disappeared" mass has been converted into $1.6 \cdot 10^{-10}$ Joules which then are released. This corresponds to 980 MeV (1 Mega electron Volt corresponds to $1.60 \cdot 10^{-13}$ J). This amount of energy can be translated into an amount of energy pr. nucleon:

$$\Delta E = \frac{-980\ \ MeV}{118\ \ neukleoner} = -8.3\ \ MeV\,/\,neukleon$$

Thus it is seen that from a thermodynamic point of view it is favourable for 50 protons and 68 neutrons to join and for a tin-118 nucleus because energy can be released. The numerical value of the energy pr. nucleon is the energy required to break down the tin-118 nucleus into free protons and neutrons. Hence the *binding energy* pr. nucleon in the tin-118 nucleus is 8.3 MeV.

1.1.5 Radioactive decay

When an unstable isotope decays it means that the nucleus changes. When this happens it is because it is more favourable for the nucleus to change and then go from a higher energy level to a lower energy level. Thus energy is released when a nucleus undergoes radioactive decay and the energy is emitted as radiation. Radioactive decay mainly results in one of the three following different types of radiation:

Alpha radiation (α radiation). The radiation consists of helium nuclei (2 neutrons + 2 protons)
Beta radiation (β radiation). The radiation consists of electrons
Gamma radiation (γ radiation). The radiation is electromagnetic radiation (photons)

When a nucleus decays and alpha radiation is emitted, the nucleus looses 2 neutrons and 2 protons which correspond to a helium nucleus. When a nucleus decays and beta radiation is emitted, a neutron in the nucleus is transformed into an electron and a proton. The electron will then be emitted as beta radiation. Gamma radiation is electromagnetic radiation which (as mentioned in section *1.1.4 Photons* on page 18) corresponds to photons. Alpha radiation is often followed by gamma radiation. When a nucleus decays it often happens in a so-called *decay chain*. This means that when a nucleus decays it is transformed into another nucleus which then again can decay into a third nucleus. This happens until a stable nucleus is formed. In the following example we will look at a radioactive decay and the emission of radiation.

Example 1- E:
Emission of alpha and gamma radiation

The uranium isotope U-238 decays under emission of alpha radiation. Such decay can sometimes be followed by gamma radiation in the form of emission of two photons. The decay can be sketched as follows:

$$^{238}_{92}U \quad \rightarrow \quad ^{4}_{2}He \quad + \quad ^{234}_{90}Th \quad + \quad 2\,^{0}_{0}\gamma$$

On the left side it is seen that the uranium isotope has 92 protons in the nucleus (corresponding to the element number of 92 for uranium). It is also seen that the uranium isotope has 238 nucleons in total in the nucleus. When an alpha particle (2 neutrons + 2 protons) is emitted the remaining nucleus only contains 90 protons and a total of 234 nucleons. When the number of protons in the nucleus changes it corresponds to that uranium has decayed into another element which in this case is thorium (Th). Thorium has the element number of 90 in the periodic table (the periodic table will be described more in details in later sections).

Alpha radiation can be followed by gamma radiation and in the case of uranium-238 decay, two gamma quantums (photons) can sometimes be emitted. These photons have different energy levels (wavelengths) and can be written as $^{0}_{0}\gamma$ since the photons has no mass at rest and no charge.