1.3 Summing up on chapter 1

In this first chapter the fundamental terms and aspects of the chemical education have been introduced. We have been looking at the single atom and its components such as the nucleus (protons and neutrons) and the surrounding electrons. The challenge in describing the motion of the electrons relative to the atomic nucleus has been introduced by use of different theories and models. These theories and models all aim in the ability to explain the different lines in the line spectra for the different elements. The atomic model derived by the Danish scientist Niels Bohr is presented and after that quantum mechanical considerations led to the viewing of electrons in motion either as particles in motion or as electromagnetic waves. From that the description of the atomic orbitals emerged. These orbitals can be visualized as areas around the nucleus with largest possibility of finding the electrons that are hosted in the orbitals. With these orbitals as a launching pad, the so-called *aufbau principle* is presented. The orbitals with the lowest energy level will be "filled" with electrons first and this leads to the construction of the periodic table. Thus the electron configurations of the elements are closely related to the construction of the periodic table. A categorization of the elements as metals, half-metals or none-metals is also given and examples of different periodic tendencies are given related to different term such as atomic radius, ionization energy, electronegativity and electron affinity.

In the next chapter we will move from the single atom to the chemical components which consist of more than one atom. We are going to look at chemical bonds and molecules.

2. Chemical compounds

In chapter 1 we saw how the elements (single atoms) are arranged in the periodic table according to in which orbitals their valence electrons are hosted. The single orbitals have been described as well. In this chapter we will among other factors use our knowledge about atomic orbitals to answer the following question:

> *Why do two hydrogen atoms join and form a H_2 molecule when for example two helium atoms rather prefer to stay separate than to form a He_2 molecule?*

We are also going to look at the geometry of different molecules by using orbital theory. That way we can among other factors find the answer to the following question:

> *Why are the atoms in a CO_2 molecule placed in a straight line (linear molecule) when the atoms in a H_2O molecule are placed in an angle (V-shape)?*

When we have been looking at different molecules we are going to move into the field of metals. In metals the atoms are arranged in lattice structures. By looking at these different lattice structures it will then be clear why metals have such high electrical conductance in all directions. We will also look at structures in solid ionic compounds like common salt which have great similarities with the metallic structures.

2.1 Bonds and forces

Initially it is a good idea to introduce the different types of bonds that hold atoms together in molecules (intramolecular forces), metal lattices and ionic lattices. After that we are going to look at which types of forces that interacts between molecules (intermolecular forces).

2.1.1 Bond types

Chemical bonds consist in that electrons from the different atoms interact and thus bind the atoms together. There are three types of chemical bonds that we are going to deal with in this book.

Covalent bonds
Ionic bonds
Metal bonds

A *covalent bond* consists in that two atoms share an electron pair. Each atom supplies one electron to this electron pair. When we are dealing with two atom of the same element we have a pure covalent bond. If the two atoms are not the same the most electronegative atom (see section *1.2.4 Perodic tendencies*) will attract the electron pair more that the less electronegative atom. Thus the electron density around the most electronegative atom will be larger than the electron density around the less electronegative atom. In this

case the covalent bond can be considered as a so-called *polar covalent bond*. When the difference in electronegativity between the two atom reaches a certain level, the electron pair will almost exclusively be present around the most electronegative atom which will then be an anion. The less electronegative atom will then be a cation since it has almost completely "lost" its bonding electron. This type of bond is called an *ionic bond* and it can be considered as consisting of electrostatic interactions between a cation and an anion rather than the sharing an electron pair. The transition from pure covalent bond over polar covalent bond to ionic bond is thus fluent which is sketched in Figure 2- 1.

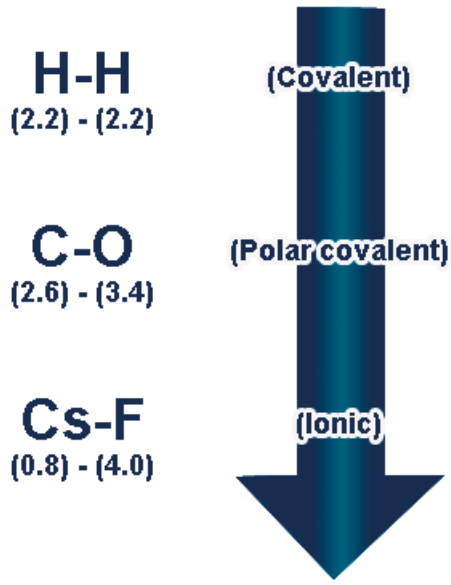

Figure 2- 1: From covalent to ionic bonds
The transition from covalent to ionic bonds is fluent and depends on the difference between the electronegativity of the atoms. The electronegativities are given in parenthesis below the sketched examples of bonds.

You have metal bonds when the metal atoms are placed in a three-dimensional lattice. In such a lattice the bond electrons "flow" around in all directions in the lattice which results in a very high electrical conductance in all directions. We have now been talking a little bit about *intramolecular* forces. The different bond types will be described in the following sections but first we are going to look at the *intermolecular* forces that interact *between* the molecules and not *inside* molecules.

2.1.2 Intermolecular forces

It is very important not to confuse the two terms *intramolecular forces* and *intermolecular forces*. Intramolecular forces are forces that act *inside* the molecules and thus constitute the bonds between the atoms. Intermolecular forces on the other hand are forces that act *outside* the molecules between molecules. The energies of chemical bonds (intramolecular forces) are much larger than the energies related to the intermolecular forces. Three different types of intermolecular forces can be distinguished:

- Dipole - dipole forces
- Hydrogen bonds
- London forces

} Intermolecular forces

Intermolecular forces to a more or minor extent hold the molecules together. If the intermolecular forces did not exist, all molecular components would be gasses. In a molecule consisting of two different atoms the bond electron pair will by average be present most around the atom with the highest electronegativity as we saw in the section *2.1.1 Bond types*. Thus we have a polar covalent or ionic bond and the molecules have a dipole moment which leads to the existence of dipole-dipole forces acting between the molecules. This will be exemplified in the following example.

Example 2- A:
Dipole-dipole forces among HCl molecules

In Figure 2- 2 the dipole-dipole forces acting between hydrogen chloride molecules in the gas state are sketched.

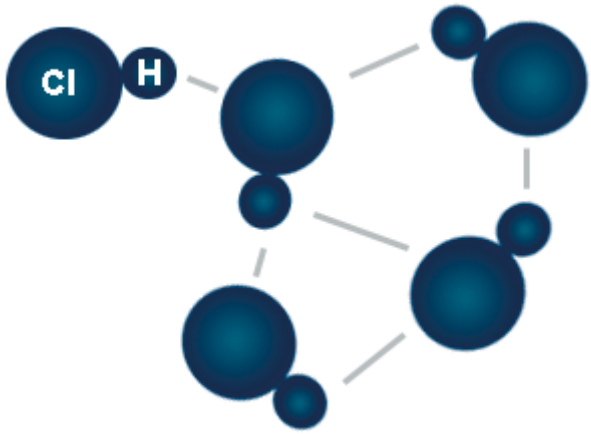

Figure 2- 2: Dipole-dipole forces among HCl molecules
The bond electron pair will by average be located most of the time closest to the chlorine atom because of the larger electronegativity. Thus the chlorine atom in the molecule constitutes a negative pole while the hydrogen atom constitutes the positive pole. Dipole-dipole interactions among the molecules are sketched by the grey lines.

The dipole-dipole forces act between the molecules because the negative end of one molecule will attract the positive end of another molecule. The dipole-dipole forces can comprise up to 1 % of the forces that act between to atoms in a covalent bond. Thus the intermolecular dipole-dipole forces are very week compared to the intramolecular covalent forces.

Hydrogen bonds are a special strong kind of dipole-dipole force. Actually hydrogen bonds are by fare the strongest kind of intermolecular forces. A hydrogen bond can comprise up to almost 20 % of the forces that exist between two atoms in a covalent bond. Hydrogen bonds can exist in the following contexts:

From an H-atom to an N-atom in the neighbour molecule
From an H-atom to an O-atom in the neighbour molecule
From an H-atom to an F-atom in the neighbour molecule

The hydrogen atom in the hydrogen bond constitutes the positive pole while the N, O or F-molecule constitutes the negative pole. In the following example we are going to look more at hydrogen bonds.

Example 2- B

Hydrogen bonds between water molecules

Hydrogen bonds play a great role in water. In Figure 2- 3 hydrogen bonds between water molecules are sketched.

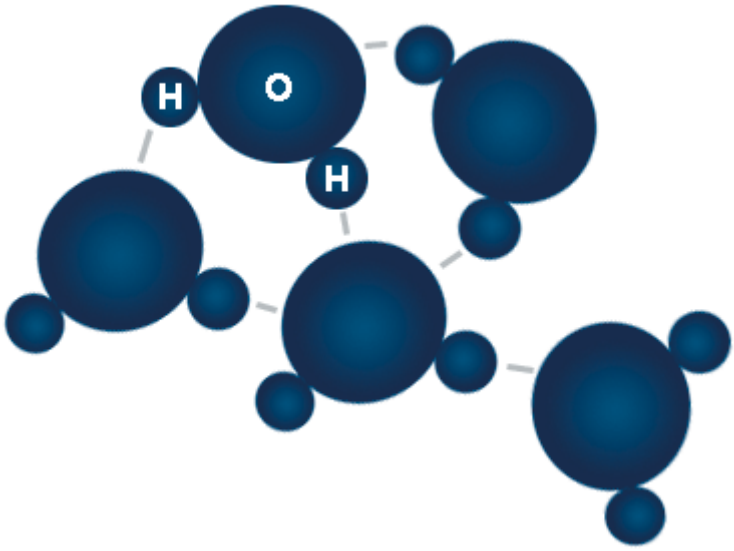

Figure 2- 3: Hydrogen bonds between water molecules

Hydrogen bonds between hydrogen atoms and oxygen atoms in neighbour molecule are sketched by the grey lines.

It is the hydrogen bonds in water that gives the relative large boiling point of water. Hydrogen bonds can comprise the energy amount of almost 20 % of a covalent bond.

Hydrogen bonds also have great biological importance since they among other factors contribute to the maintenance of the helical structure of DNA-molecules.

London forces are named after the German-born scientist Fritz London. London forces are a type of forces that exists among *all* kinds of molecules. While dipole-dipole forces only acts between molecules with dipole moments and hydrogen bonds only acts between molecules containing hydrogen and either nitrogen, oxygen or fluor, London forces act between *all* kinds of molecules. It is the London forces that bind molecules which on the outside appears unpolar (no dipole moment) together. The electron cloud that surrounds an atom or a molecule with no dipole moment will on an average be equally distributed around the whole atom or molecule. But if you look at the electron cloud at a specific time, the electron cloud will be displaced. You can say that the electron cloud “laps” around the atom or molecule like waves at the oceans thus inducing momentarily dipole moments. These momentary dipole moments can momentary interact with the momentary dipole moment in the neighbour molecule. These interactions are called London forces and in the following example we are going to look at the London forces that act between hydrogen molecules.

Example 2- C:
London forces between hydrogen molecules

Hydrogen molecules on the outside have no dipole moments. Even so some forces act between the hydrogen molecules. These forces are the London forces and they exist because the electron clouds in the hydrogen molecules "laps" around and induce momentary dipole moments that momentary can interact with each other and thus "drag" the molecules together. This is sketched in Figure 2- 4.

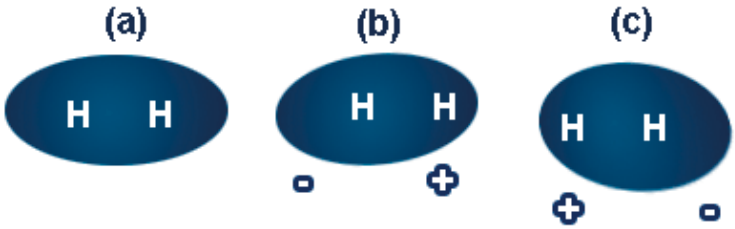

Figure 2- 4: London forces between hydrogen molecules
(a) By average the electron cloud is located equally around the H-H bond. Thus by average there is no dipole moment. (b) At a given time the electron cloud will be displaced so that that there will be a momentary dipole moment. (c) At another given time the electron cloud will be displaced in another way so that a "new" dipole moment will be induced. Interactions between momentary dipole moments are called London forces.

The more electrons that are present in the molecule the more electrons can "lap" around and the larger momentary dipole moments can be induced. Therefore London forces are larger between larger molecules.

Till now in this chapter we have very briefly been looking at the different types of bonds that can exist between two atoms (intramolecular forces) and at the different types of forces that can act between molecules (intermolecular forces). In the following sections we are going to look more detailed into the different types of chemical bonds. That way we among other aspects will be able to explain why it is beneficial for some atoms to join in a chemical bond and why this is not the case for other atoms.

2.2 Covalent bonds

In this section we are going to look at the nature of the covalent bonds.

Why do covalent bonds form?
Which structures do molecules with covalent bonds presume?

These questions and other aspects concerning energy considerations, molecular orbital theory, Lewis structures, VSEPR theory and orbital hybridization theory will be answered and covered in this section.

2.2.1 Energy considerations

When two atoms join and form a molecule by creating a covalent bond, it always happens because in terms of energy it is favourable. The total energy can be lowered by creating the covalent bond and this is the reason that the bond is formed.

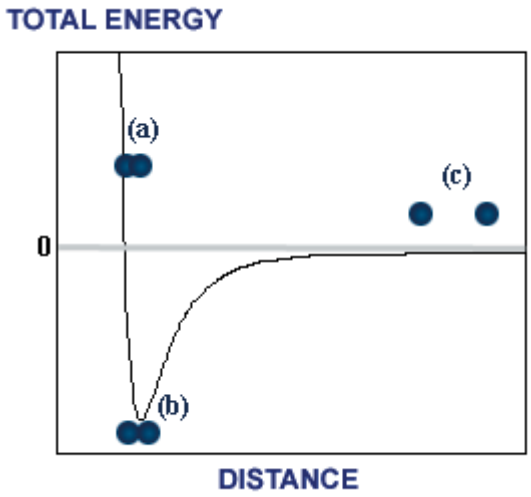

Figure 2- 5: Energy profile
The total energy between two hydrogen atoms as a function of their distance. (a) When the two hydrogen atoms are force close together the potential energy increases very dramatic similar to when two north pole magnets are forced together. (b) At a certain distance (which is the bond length) between the two hydrogen atoms there is a minimum in energy. (c) When the two hydrogen atoms are fare away from each other the energy is zero which corresponds to no bonding.

In the graph on Figure 2- 5 it is seen that at a certain distance between the two atomic nuclei the total energy has a minimum. This distance corresponds to the bond length of the covalent bond between the atoms. When the two atoms are fare apart from each other the total energy is zero which corresponds to the existence of no bond at all. If the two atoms are forced together (closer together than the bond length), the total energy will increase dramatically and the atoms will repeal each other. This can be compared to when two north pole (or south pole) magnets are forced together. The potential energy will increase very much and they will repeal each other.

2.2.2 Molecular orbital theory

The energy profile in Figure 2- 5 shows that at a certain distance between the atoms there is a minimum in energy which just corresponds to the bond length of the covalent bond. However we still know nothing about how and where the two electrons of the bonding electron pair are placed. It is also seen in Figure 2- 5 when going from the right to the left that when two atoms approach each other the energy will be minimized when approaching the bond length. How can this be explained? *Molecular orbital theory* can be used to explain why some atoms form molecules and why others do not[1].

When two atoms approach each other the atomic orbitals will ”melt” together and new so-called *molecular orbitals* will be formed. In these molecular orbitals the bond electrons of the covalent bond will be hosted. There are two types of molecular orbitals:

Bond orbitals, denoted with the Greek letter σ
Anti-bond orbitals, denoted with σ^*

The bond orbitals have lower energy levels compared to the anti-bond orbitals. As for the atomic orbitals these molecular orbitals are each able to host two electrons. In the following example we are going to se how the atomic orbitals of two hydrogen atoms “melt” together and form two molecular orbitals during the formation of a hydrogen molecule.

[1] When we are talking about orbitals (as in chapter 1) it is initially important to notice that we are talking about mathematical models that are able to explain different physical and chemical phenomena. It is not necessarily evidenced that the actual physical and chemical conditions are in agreement with the models but the models are just efficient in explaining certain behaviors, tendencies and conditions.

Example 2- D:
Molecular orbitals in the hydrogen molecule

The hydrogen molecule is here used as an example since it is relatively simple because the number of electrons is only 2 in total. Each (valence) electron of the hydrogen atoms is hosted in a 1s-orbital when the two atoms are single. When the two 1s-orbitals approach each other, two new molecular orbitals are formed; one bond orbital and one anti-bond orbital which is sketched in Figure 2- 6.

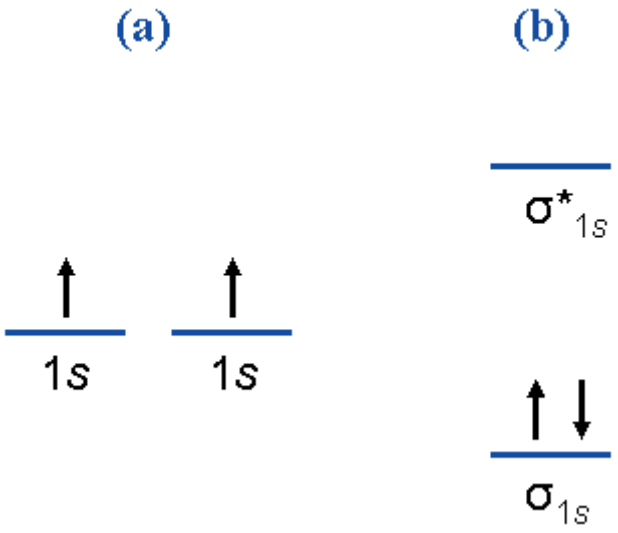

Figure 2- 6: Molecular orbitals in the hydrogen molecule
(a) The two atomic orbitals (1s) when the atoms appear in single (b) The two atomic orbitals "melt" together and two molecular orbitals are created. One of the molecular orbitals is a bond orbital (σ_{1s}) and one is an anti-bond orbital (σ^*_{1s}).

Since the molecular bond orbital (σ_{1s}) is lower in energy level at the two individual atomic orbitals, the two valence electrons rather prefer so stay in the bond orbital. The energy level of the anti-bond orbital (σ^*_{1s}) is higher than that of the atomic orbitals and thus the valence electrons will no be hosted in this orbital.

So because the total energy can be minimized it is beneficial for the two hydrogen atoms to create a hydrogen molecule.

A covalent bond can be assigned with a so-called *bond order* according to the following equation:

$$Bond\ \ order = \frac{\left(electrons\ \ in\ \ bond\ \ orbitals\right) - \left(electrons\ \ in\ \ anti-bond\ \ orbitals\right)}{2} \qquad (2\text{- }1)$$

The bond order is related to the bond energy. The larger bond orders the larger bond energy. In the case with the hydrogen molecule (Figure 2- 6 on page 54) there are two electrons in the bond orbital σ_{1s} and zero electrons in the anti-bond orbital σ^*_{1s}. This gives the covalent H-H bond a bond order of 1 and it corresponds to a *single bond.* If the bond order would have been 2 (corresponding to a *double bond*) the bond energy would have been larger. In the following example we find out why two helium atoms do not join and form a helium molecule (He_2).