Chemical Bonding: Intramolecular and Intermolecular Bonds

In general, it is possible to distinguish between intramolecular and intermolecular bonds. The first group includes the ionic bond, atomic bond, and metallic bond. The second one includes the Van-der-Waals-bond and hydrogen bridges. These bonds have an important influence on the substance properties, such as solubility.

Intramolecular Bonds

Ionic bonding

Ionic bonding is a type of chemical bond that is based on the force of attraction between oppositely charged ions (Coulomb-force, electrostatic force). Due to the ionic bond, there occurs a regular arrangement of ions, which is also called ionic crystal. If a solid is built up by ions, then it is considered a salt. They are weaker and less stable but still abide by the octet rule. Common table salt (NaCl) is formed by ionic bonds.

- First ions are formed then the ions are attracted by their opposite charge.
- Sodium (Na) has 1 valence electron – could lose 1 (easy) or gain 7 (difficult).
- Chlorine (Cl) has 7 valence electrons – could gain 1 (easy) or lose 7 (difficult).
- CI steals the electron from Na to satisfy the octet rule – resulting in ions.
- CI\(^{-}\) is now attracted to Na\(^{+}\).
- This will come apart in water.

The following are the **common characteristics of an ionic crystal**:

- Regular, grid-like, spatial arrangement
- Positively charged metal ions and negatively charged non-metal ions
- Strong forces of attraction
- Relatively high melting and boiling temperature
- Brittle
- No electrical conductivity of the solid
- Good electrical conductivity of the molten, and of the aqueous solution

**Atomic bond (covalent bond)**

An **atomic bond** is a type of chemical bond that is **based on the formation of a common electron pair**. The atoms have solid partners, referring to a directed binding. Single covalent bonds involve the sharing of one pair of electrons. Hydrogen has a valence of 1 & 1 valence electron; 2 electrons in the valence shell will satisfy the octet rule. Each has 2 electrons in the valence shell.

Double covalent bonds involve the sharing of two pairs of electrons (stronger). Oxygen has 6 valence electrons. It needs 2 more electrons to satisfy the octet rule. It shares 2 electrons with another oxygen. They have 2 pairs of shared electrons in this bond. The substance class of molecular substances can be derived from this type of binding.
They have 2 pairs of shared electrons in this bond. Each oxygen has 8 electrons in the valence shell (stable).

Substance properties: Relatively low melting and boiling temperature.

**Metallic bond**

The metallic bond is a type of chemical bond that is based on the forces of attraction between positively charged metal ions and negatively charged, versatile ions. The substance class can be derived from this binding type.

Characteristics: regular, a grid-like arrangement of the positively charged metal ions in a space

Substance properties:

- Mostly solid (except mercury)
- Metallic lustre
- Good electrical conductivity (which decreases with an increase in the temperature)
- Good thermal conductivity
- Plastically deformable

Calculation: Not calculable, as it occurs in metals and alloys.

**Hydrogen bonds**

Hydrogen bonds form between polar molecules:

- Slight negative charge by the oxygen of H₂O
- Slight positive charge by the hydrogens
- Causes attraction between them
Intermolecular Bonds

Van-der-Waals-bond

The Van-der-Waals forces represent weak forces of attraction or non-covalent interactions between molecules, atoms or ions. It is dependent on the particular size and the contact surface.

Hydrogen bridges

If **two molecules interact via a hydrogen atom**, then so-called hydrogen bridges occur. Strong forces of attraction are formed between the positively charged hydrogen atom, and a free electron pair of a nitrogen, oxygen or fluorine atom. Hydrogen bridges are only formed with the most electronegative elements (N, O, and F). At this, there is a donor and an acceptor.

In case of the donor, the hydrogen atom is bonded to a highly electronegative partner, whereby the hydrogen atom becomes the positive pole (positive partial charge) and the binding partner becomes the negative pole. The acceptors are generally covalently bonded nitrogen, oxygen or fluorine atoms, which possess a negative partial charge.

Relevance of the hydrogen bridges in the biochemistry:

- **DNA**: Base pairing, an amalgamation of the DNA strands
- **RNA**: tRNA (formation of intramolecular hydrogen bridges)
- **Proteins**: Formation of secondary structures (α-helix, β-sheet)

Other Sigma Bonds

Sigma bonds

Sigma bonds are types of bonds in a molecular structure that are formed by end-to-end overlap of atomic orbitals. Unless this type of overlap is possible, a sigma bond may not form. One simple sigma bond is the one present in an H₂ molecule. Since an H atom only has an s-orbital, the overlap will be between two s-orbitals.

Overlap between two p-orbitals is also possible. To form a sigma bond, the interaction should be a head-to-tail interaction, which is one lobe of one p-orbital faces one lobe of the other p-orbital, enabling the overlap as in the figure below.

Sigma bonds may also be formed by the interaction of dissimilar orbitals. In the case of the bond between Hydrogen and Fluorine in hydrogen fluoride, the H atom only has an s-orbital available for bonding, while the F atom has a p-orbital. Even though the two
orbitals are different, a sigma bond may still be formed as long as the two interacting orbitals are in the correct orientation. In this way, sharing of electrons will be achieved between the two atoms.

For example, if the s and p-orbital interacting with each other are in an orientation where one of the lobes of the p-orbital is directly facing the s-orbital, a sigma bond may form because overlap of orbitals is possible. If the s-orbital of the H atom is not directly facing any of the two lobes of the p-orbital, no sigma bond will be formed because orbital overlap will not occur.

Hybridization

For heteroatomic molecules, the overlap of simple s and p-orbitals will result in a highly restricted molecular structure. For example, the compound methane does not follow an ordinary square planar structure; instead, it follows a tetrahedral configuration. Also, since the p-orbitals are oriented in different planes, this would involve different energy values. To aid this, hybridization should occur. Orbital hybridization is the mixing of atomic orbitals into new hybrid orbitals, with different shapes and energies to the component atomic orbital, suitable for electron pairing during the formation of covalent bonds.

In a methane molecule, it is not possible to form four sigma bonds due to 1 s-s and 3 s-p interaction. This is because they will have different amounts of energy involved. What happens then is the one s and the 3 p-orbitals of the C atom will be hybridized to form 4 sp³ hybrid orbitals that are all similar in energies and shapes. Each of these sp³-orbitals will overlap with the s-orbital of an H atom forming four sigma bonds, resulting in a tetrahedral configuration.

Different types of hybrid orbitals may be formed, depending on the type of atomic orbitals that combine. If one s and one p-orbital are mixed, two sp hybrid orbitals are formed. On the other hand, if one s and two p orbitals are mixed, three sp² orbitals are formed. The number of hybrid orbitals corresponds to the number of sigma bonds that the atom can form. For example, if an atom has two sp hybridized orbitals, this means it can form two sigma bonds. The same case is if an atom has three sp³ hybridized orbitals, three sigma bonds can be formed.
Between two atoms, only one single bond is possible to be formed. This is because there is only one way for end-to-end interaction to occur, especially since the p orbitals are oriented in different planes. Another type of orbital overlap is possible. If two p-orbitals are oriented parallel to each other, a side-by-side overlap is possible. This type of interaction leads to the formation of pi bonds.

Pi bonds are weaker than sigma bonds because of the weaker overlap between the orbitals. Electrons in pi bonds can also be referred to as pi electrons. Pi bonds are present in multiple bonds (double or triple bonds). Pi interaction is only possible between atoms that are already sigma bonded.

In the case of the compound ethene, three sigma bonds are formed by each of the C atoms. This means that 3 hybrid orbitals were used. This is only possible if 1 s and 2p-orbitals have undergone hybridization. This means each of the C atoms will have an extra p-orbital that can overlap with the p-orbital of the other C atom to form a pi bond.

Double and triple bond

Double bonds and Triple bonds only differ in the number of pi bonds present in the bond. A double bond will contain one sigma bond and one pi bond, while a triple bond contains one sigma bond and two pi bonds.

There is a correlation between the type of hybrid orbital and the type of bond present around an atom. A carbon compound with the C atom containing 4 sp³-orbitals can form 4 sigma bonds. A carbon compound with the C atom containing 3 sp²-orbitals and one p can form 3 sigma bonds and 1 pi bond. A carbon with the C atom containing 2 sp-orbitals and 2 p-orbitals can form 2 sigma bonds and 2 pi bonds. This leads to the formation of double and triple bonds.

Review Questions

The correct answers can be found below the references.

1. How many sigma and pi bonds are present in the ethyne (C₂H₂) molecule?
   A. 2 sigma, 3 pi bonds  
   B. 3 sigma, 2 pi bonds  
   C. 2 sigma, 2 pi bonds  
   D. 3 sigma, 1 pi bonds

2. What is formed when 2 p and 1 s-orbitals are mixed during hybridization?
A. sp
B. sp²
C. sp³
D. Nothing will happen.

References


Correct answers: 1B, 2B

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