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BASICS OF CHEMISTRY

CHAPTER 1

INORGANIC CHEMISTRY

1.1 – *The atomic structure of matter*

It is today accepted and well known by everybody that matter hasn't a continuous structure.

Contrary to the direct impressions of our sensations (macroscopic impressions leading to the assumption that matter has a continuous and geometric structure, without empty spaces), in the reality solid, liquid and gaseous bodies are constituted of a very large number of elementary units, distinct each other and characterized by individual properties.

The atom, a particle of extremely small dimension in comparison with those we are more familiar with, is the fundamental unit of matter.

The atom has a dimension of about 10^{-8} cm which is well below the resolution of the most powerful optical and scanning electron microscopes. A pin-head, whose dimension represents the resolution (defined as the smallest distance between two points on a specimen that can still be distinguished as two separate entities) power of an human eye (about 1/10 mm or 100 microns), has a size that would contain about one million atoms.

The name atom comes from the Greek ἄτομος (*atomos*, "indivisible"), which means uncuttable, or indivisible, something that cannot be divided further. During the late 19th and early 20th centuries, physicists discovered subatomic components and structure inside the atom, thereby demonstrating that the 'atom' was divisible. The concept of indivisibility can actually be applicable as long as the uniqueness of matter relates with what we macroscopically touch, see, smell and call matter. However, atoms as well has their own internal structure.

The existence of this fundamental unit of matter accepted, it is clear that matter should be constituted by different atoms because it appears so different in forms, shapes, colours, smells and other properties. In fact, atoms aren't all the same but differ each other. For example, atoms have different weights.

There exist different atoms the weight of which is only a consequence of their different atomic structure.

1.2 – *Chemical elements, compounds and mixtures*

Any solid, liquid or gas body consists of chemical elements, which are pure chemical substances consisting each of one type of atom. Chemical elements are commonly represented by *chemical symbols*.

Familiar examples of elements include Iron (chemical symbol Fe), Carbon (C), Chlorine (Cl), Sulphur (S), Oxygen (O), Aluminium (Al), Mercury (Hg) and Chromium (Cr). In their pure form each of these substances consist of one type of atom.

Since, as we already said, atoms have also different weights (that is each element is identified by a specific weight) there should be a chemical element whose atoms weight less than the others and represents the lower limit of the series.

This chemical element is Hydrogen (H). Starting from hydrogen and taking into consideration the progressively heavier elements, we might logically ask how far we can go with the weight increase of atoms. Since there isn't an apparent reason that limit the weight increase, should we expect to have an infinite series of atoms? The answer is not. The internal structure of atoms and their constitution doesn't allow a certain limit of complexity to be exceeded and, hence, a weight increase. Above a certain weight limit an atom becomes unstable, tending to disintegrate.

The elements consisting of stable atoms are 92; they are called *natural* elements. The elements above Uranium, which is the element 92 and the heavier of this series, have unstable atomic structures and are called *transuranium* (or *transuranic*) elements. They do not occur naturally on Earth but have been produced artificially as the synthetic products of man-made nuclear reactions. As of November 2011, 118 elements have been identified, the latest being ununoctium in 2010.

Apart from the artificially made elements, which are of scarce direct interest (many of them play a crucial role in nuclear physics), we can state that all matter consists of only 92 atomic species.

However, what said above doesn't fully explain the great variety of properties shown by the matter. In fact, if substances would consist of atoms of the same type, only 92 substances would be present in nature; perhaps 118, if we also consider the transuranium atoms.

On the contrary a very large number of substances exist in nature and it continuously increase. How all this is possible?

Simply speaking different atoms link each other in some way and in different proportions to constitute polyatomic aggregates, the substances, behaving as many elementary units of matter.

These aggregates (at least diatomic, constituted of two different atoms or sometimes same atoms, held together by chemical bonds) are called *molecules*.

A molecule is therefore the smallest part of matter that keeps the chemical and physical properties of a substance consisting of one or more elements. Hence, substances consisting of different atoms are called *compounds*.

Therefore, matter consists of elements and compounds that are also called "chemical moieties" because of their well identified chemical nature.

To sum up:
- ✓ there are different type of atoms
- ✓ atoms of the same type constitute the chemical elements
- ✓ different atoms held together in well defined and constant proportions constitute the compounds

Finally, a *mixture* is obtained by mixing up together two or more substances in any possible proportions. Mixtures do not constitute new compounds as each component retain its individual characteristics; the example of a mixture of Iron (Fe) and Sulphur (S) is well known. At room temperature, particles of Iron and Sulphur can be mixed each other without producing a new molecule, as no chemical bonding is

established between the two elements. In fact, by means of a magnet, Iron can be easily mechanically separated from Sulphur. On the other hand, by heating the mixture a chemical bonding between the two element is established, and a molecular compound, named iron sulphide (FeS), is created; this compound is a new substance characterized by properties different from those of the single elements iron and sulphur.

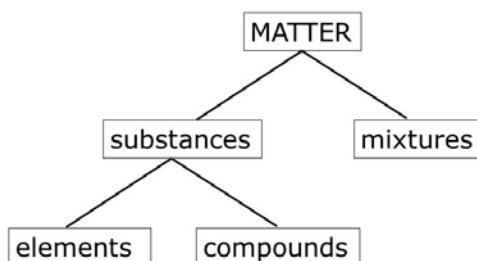A schematic drawing of matter and its components is presented in figure 1/1.

Fig. 1/1 – Components of matter

1.3 – *Atomic structure*

In light of contemporary atomic theories an atom can be schematically represented in the following way. All atoms are composed of a central *nucleus* within which almost all the mass of the atom is concentrated. An atomic nucleus is the small heavy central part of an atom consisting of nucleons: *protons* and *neutrons*. Protons are subatomic particles and a positive electric charge of 1 elementary charge, whereas neutrons are subatomic particles which have no net electric charge and masses slightly larger than that of protons.

The positive charge of the nucleus is neutralized by subatomic particles with a negative elementary electric charge surrounding the nucleus, having masses that are approximately 1/2000 that of protons, called *electrons*.

In normal conditions, an atom is electrically neutral, that is it carries no electrical charge and contains the same number of electrons and protons.

For example the simplest and lightest atom is hydrogen (H) that contains only one proton and one electron and can be schematically represented as a sphere; the proton is located in the centre whereas the electron rotates with high speed on the surface.

Let now consider an atom that we name D, whose nucleus consists of one proton and one neutron. Since the atom is electrically neutral, the overall charge is neutralized by only one electron. Moreover, since the proton and the neutron have almost the same mass and the weight of the electron is negligible, this atom weights double the hydrogen.

We could ask ourselves: is this another type of atom?

Before answering this question, we could consider (at least theoretically) a third atom consisting of two protons neutralized by two electrons; this atom would weight double an hydrogen atom and would have the same mass of the above mentioned atom D.

This third atom and the atom D, though having the same mass, are two different species. The atom D is instead of the same type of the hydrogen atom, although has a double mass.

In fact, what makes atoms different each other and determines the chemical elements to which they belong, is not their weight (or, more precisely, their mass) but the *number of protons they have within their nucleus*.

To sum up, two atoms, though having the same mass, can belong to different chemical elements, if they have a different number of protons; on the other hand, independently from their mass, two atoms belong to the same chemical element when they have the same number of protons, to which an equal number of electrons corresponds.

However, because the number of electrons involved in chemical reactions can vary, each single atom is specifically identified only by the *number of protons* it contains in the nucleus: *atomic number* is the name given to this number and each chemical element has its own atomic number. Therefore, the only rigorous criteria to follow in the classification of elements is to arrange them by order of atomic number in a way that their periodic properties (chemical periodicity) are made clear.

To this purpose a periodic table of the chemical elements was first conceive by the Russian chemist D. Mendeleev and includes periods (usually horizontal in the periodic table) and groups (usually vertical). Elements in groups have some similar properties to each other (Figure 1/2) which result directly from the arrangement of the electrons moving around the external orbitals.

Fig. 1/2 – The periodic table of the chemical elements

The previously discussed example of atom D is of course just a theoretical example, because actually it doesn't exist. In fact, the two protons, both positively charged, couldn't exist alone (they would experience a mutual repulsive force) without the contemporary presence of subatomic particles, which have no net electric charge,

called neutrons. A given atom generally consists of a number of neutrons equal or slightly higher that protons; however, it isn't as much constant for all atoms of an element.

In practice a single element cab be characterized by more than one atomic structure consisting of the same number of protons (and hence of electrons) but different number of neutrons. These variations do not affect the chemical properties of the element (that remain to be defined by the number of protons) but only its nuclear properties.

The variants of atoms a particular element can have are called *isotopes*: atoms of a particular element must contain the same number of protons but may have a distinct number of neutrons which differ from atom to atom, without changing the designation of the atom to a particular element. When the number of neutrons, in relation with that of protons, exceeds certain limit values an unstable atomic structure is produced, leading to *radioactive disintegration* phenomena. The case of the element Carbon(C) is given as an example.

C_6^{12} (6 is the atomic number and 12 is the mass number, that is the number of particles present within the nucleus: in this case 6 protons and 6 neutrons) and C_6^{14} (6 protons, but 8 neutrons) are two isotopes of the element carbon. C^{12} isotope is stable and abundant in nature, whereas C^{14} is unstable and hence radioactive. The presence of C^{14} in organic materials is the basis for the radiocarbon dating method to date archaeological and geological samples.

Another important chemical term of fundamental importance in chemistry is *atomic weight*, a dimensionless physical quantity based on the ratio of the average mass of an element to 1/12 of the mass of a C^{12} atom (known as *unified atomic mass unit*).

You will notice that atomic weights are often expressed not as whole numbers but as decimals, and this is quite easy to guess as they result from the average of the different isotopes of a given element present in nature.

In the case of a molecule, consisting of more atoms, the *molecular weight* is determined by adding up the atomic weights of the atoms constituting the molecule:

For example, the calculation of the molecular weight of a gypsum molecule, consisting of di-hydrate calcium sulphate with the formula $CaSO_4 \cdot 2H_2O$, has to be made by adding up the individual atomic weights of all atoms in the molecule:

Chemical element	Atomic weight
Ca (calcium)	40,08
S (sulphur)	32,064
O (oxygen)	15,999
H (hydrogen)	1,008

The molecular weight will be

Chemical element	Atomic weight
Ca: 1 atom	40,08
S: 1 atom	32,064
O: 6 atoms	95,994

	H: 4 atoms	4,032
Molecular weight	CaSO$_4$•2H$_2$O	172,170

It is worth mentioning that both atomic and molecular weights are dimensionless as they represent weight ratios indicating how many times an atom is heavier than the unified atomic mass unit.

In chemistry there are two important units, the mole and the gram-atom that are used to express the relative quantities of reactants and products in chemical reactions. The number of molecules in a mole (known as Avogadro's number) is defined so that the mass of one mole (the term gram-molecule was formerly used) of a substance, expressed in grams, is exactly equal to the substance's mean molecular weight. On the other hand, the gram-atom is the quantity of a substance that contains Avogadro's number of atoms. Thus, for example, 1 mole of H$_2$O is 3 gram-atoms of H$_2$O.

1.4 – *Orbitals, electronegativity, chemical bonds*

All atoms are composed of a central *nucleus* carrying a positive charge surrounded by electrons that carry a negative charge. But where these electrons are located?

According to quantum theory, we can never know the exact position of an electron as it moves around the nucleus within an *atomic orbital* which is a mathematical function that refers to the physical region where the electron can be calculated to be.

According to their shape, there exist *s*, *p*, *d* and *f* orbitals. These names indicate the orbital shape and are used to describe the electron configurations of an atom. There might exist 1 *s* orbital, 3 *p* orbitals, 5 *d* orbitals and 7 *f* orbitals. Each orbital can contain a maximum of two electrons. Table 1 reports for each orbital the maximum number of electrons it can host.

type of orbital	number of orbitals	max electrons the orbital can host	atomic shell
s	1	2	K
p	3	6	L
d	5	10	M
f	7	14	N

Tab. 1/1 *Orbitals, number of electrons and atomic shells*

Around each nucleus the orbitals are organized in layers called *shells*. The closest shell to the nucleus is called "K shell", followed by "L shell", then "M shell" and so on further and further from the nucleus. Each shell can contain only a fixed number of electrons; thus, for example, the K shell hold up 2 electrons, the L shell can hold up

8 electrons in its four orbitals, the M shell can hold up 16 electrons and so on so for. The electrons in the partially filled outermost shell determine the chemical properties of the atom (this is called *valence shell*), that is its tendency to establish bonds with atoms of the same type or with other atoms to form molecules.

Before getting into the discussion of chemical bonds we need to introduce the concept of electronegativity.

As we said, the tendency of an atom to acquire or to donate electrons located in its outermost is at the origin of all bonds between atoms. Electronegativity is a chemical property that describes the tendency of an atom to acquire more electrons in order to fill completely its outermost shell (electronegative atom); an atom that has only few electrons tends to donate them in order to create an empty shell (electropositive atom). Electronegativity is a dimensionless quantity ranging from around 0.7 to 3.98 (referred to as the Pauling scale) and cannot be strictly considered a property of an atom, but rather a property of an atom in a molecule. In general, electronegativity increases on passing from left to right of the periodic table of the elements and decreases on descending a group. Less electronegative chemical elements are said to possess a "metallic character", whereas highly electronegative elements possess a "non-metallic character".

Let now discuss the different chemical bonds that can be established between atoms.

Covalent bond

The covalent bond is formed between atoms having approximately the same electronegativity by sharing the electrons of their outermost shell.

For example, an hydrogen atom contains one single electron in its single and outermost orbital; this atom, in order to reach a stable electron configuration (2 electrons in the *s* orbital) will have the tendency to complete it, attracting another electron.

Therefore, two hydrogen atom may complete their respective orbitals by sharing their single electrons. In fact, because the two atoms are the same and have the same electronegativity, there isn't any tendency for one of them to preferentially attract the electron of the other. This results in the sharing of the electrons between the two hydrogen atoms and the formation of an orbital, called *molecular orbital*, containing two electrons, which determines the establishment of a strong covalent bond. This type of bond may be represented graphically as the overlapping of two orbitals, each containing one electron only.

Polar covalent bond; dative covalent bond (or dipolar bond)

Let now consider two atoms with different electronegativity. A bond can again be established by sharing their electrons located in their outermost shells. However, because of their different electronegativity, the two electrons are not equally shared between the two atoms but they tend to be closer to the more electronegative atom; as a consequence the less electronegative atom remains with a slight excess of positive charge. This couple of electric poles joined by a bond is called *dipole* and a *polar covalent bond* is, therefore, formed between the two atoms.

In general, the covalent polar bond is due to electrons belonging each from the single atoms involved in the bond. However, it may happen that the two electrons belong both from only one of the two atoms involved. The bond established in this way is called *dative covalent bond*, which differs from the polar covalent bond in the way it is formed.

The polar covalent bond (asymmetric molecular orbital) differs from both the pure covalent bond (symmetric molecular orbital) and the ionic bond that will be discussed in the next paragraph. In fact, the electrons involved in the polar covalent bond aren't completely transferred from one atom to the other as it happens with the ionic bond but, as already said above, they just tend to be closed the more electronegative one. The polar covalent bond is the more diffused type of bond and can be considered in-between a ionic and a pure covalent bond; in fact, the probability that the high difference in electronegativity needed for the establishment of a ionic bond or the similar electronegativity needed for the establishment of a pure covalent bond is lower than the polar covalent bond requirements.

Ionic bond

When the electronegativity of two atoms is very different the bond isn't anymore formed through the sharing of electrons, but they are rather preferentially transferred to the more electronegative atom. In this way the two atoms become electrically charged because in both atoms the number of positive charges (nucleus) does not match the number of negative charges (electrons). These chemical species are called *ions*. There may exist *anions*, consisting of atoms having an amount of electrons exceeding the number of protons (therefore negatively charged) and cations consisting of atoms that lost electrons (positively charged). The bond that can be formed between the two is called *ionic bond*; it greatly differs from the bonds we have been discussing so far and can be described as the result of the establishment of an *electrostatic interaction* between two or more ions.

Ions can be represented graphically as spheres whose electric charges are homogeneously distributed along the overall surface so that the electric force of attraction is exerted in all space directions. As a consequence, the concept of molecule cannot be applied, as it is not a couple of ions that is formed but rather a *ionic crystal*, that is a regular, ordered and tri-dimensional structure of billions and billions of ions.

Metallic bond

The metallic bond is based on the sharing of the electrons of the outermost shell by a large number of atoms of the same metal element. It can be represented as a situation in which single atoms are surrounded by the electrons of the neighboring atoms to which they are linked. Generally speaking, we can say that each atom shares with the others both the unpaired electrons and their respective orbitals. The superimposition of these orbitals results in the formation of an orbital, extended to all atoms (electronic cloud), within which electrons are free to move. This is the *metallic bond* (the term *metallic bonding* seems to be more appropriate as this type of bonding is collective in nature and a single metallic bond does not exist).

Such a distribution of electrons implies the metal atoms to arrange themselves in the closest packed structure, that is a crystalline type structure that accounts for the many physical properties of metals, such as strength, malleability, ductility and thermal and electrical conductivity.

1.5 – *Intermolecular bonds. Hydrogen bond*

The covalent bonds (pure covalent and polar covalent bond) that are established between atoms of the same molecule are called *intramolecular bonds*.

However, attractions may also exist between one molecule and a neighboring molecule. These attractions, which are weaker that bonds between atoms and can be exerted in different ways and according with the nature of the molecules involved, are called *intermolecular bonds*.

Most of the chemical-physical properties of matter and most of the phenomena in which is involved, directly depend on the type and strength of these interactions.

The full understanding of intermolecular bonds is an issue of particular interest in chemistry for restoration, which always involves solubilization, adhesion, cohesion and transition states processes. Different type of intermolecular bond can be identified:

a) *interaction between polar molecules*

a polar molecule is a molecule in which the centre of positive charge does not coincide with the centre of negative charge because the set of intramolecular attractions are not balanced in polarity.
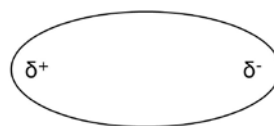
Lozenge-shaped diagram representing a dipole molecule or dipole

Between two or more dipole molecules electrostatic attraction forces can obviously be exerted, leading to dipole-dipole intermolecular bonds (Fig. 1/3)
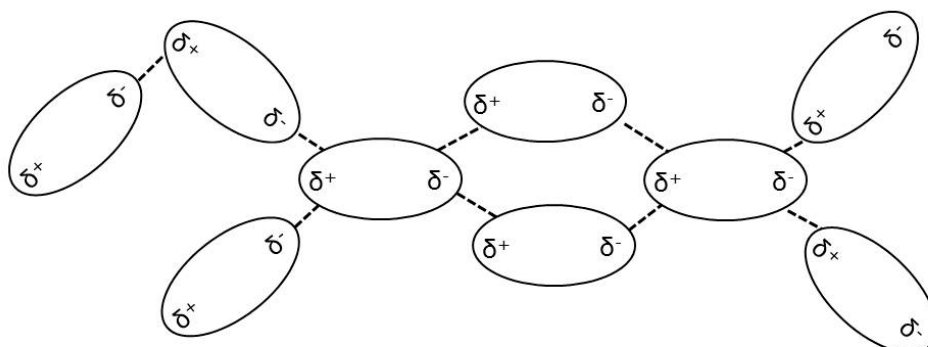
Figure 1/3 – Schematic drawing of attraction forces among dipole molecules

b) interaction between non-polar molecules

a nonpolar molecule is a molecule which has no separation of charge, so no positive or negative poles are formed. In spite of that, nonpolar molecules can be attracted each other through weaker forms of intermolecular attractions called *van der Waals dispersion forces*. This term includes different type of forces, all characterized by the absence of an electrostatic character.

c) hydrogen bond

When an hydrogen atom is covalently bonded to highly electronegative atoms such as nitrogen, oxygen, fluorine and chlorine an attraction force between the lone pair of the electronegative atom and hydrogen is created.

The proton that in this case is almost free, exerts through its positive charge strong attraction forces towards the negative pole of the neighboring molecules. In fact, the hydrogen bond is often described as a strong electrostatic dipole-dipole interaction, even though it also has some features of covalent bonding.

The simplest example of a hydrogen bond is found between water molecules:

the O-H bond of water is a covalent bond and, moreover, the hydrogen is bonded to oxygen, an highly electronegative atom. Such a situation allows the formation of an hydrogen bond.

The resulting hydrogen bond has an high polar character; in fact, oxygen is negatively charged whereas hydrogen carries a positive charge. This allows the establishment of attraction forces between the hydrogen of a water molecule and the oxygen of another water molecule (Fig. 1/4).
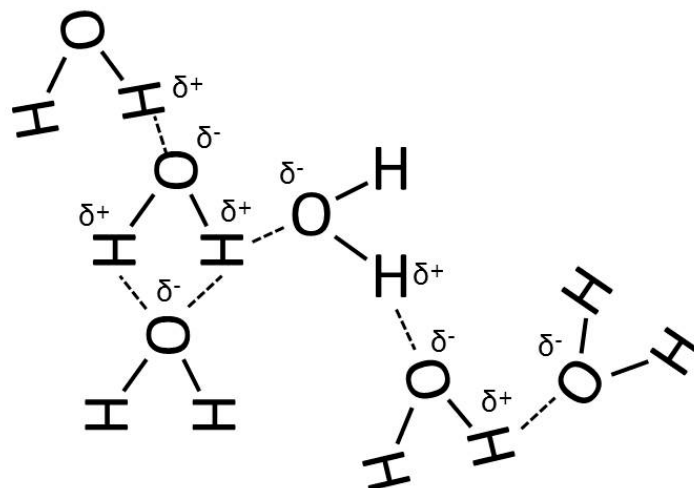

Figure. 1/4 – Schematic drawing of hydrogen bonds between molecules of water (dashed lines indicate hydrogen bonds)

The chemical and physical properties of substances are strongly affects by the presence of hydrogen bonding. For example, liquid water's high boiling point is due to the high number of hydrogen bonds each molecule can form relative to its low molecular weight.

In macromolecules such as proteins and cellulose, hydrogen bonds can be established internally to the molecule through the formation of the so called intramolecular hydrogen bonds.

1.6 – *Valence, oxidation number and oxidation state*

Valence (or valence number) is a measure of the number of possible bonds an atom of a given element can form and it is of great importance in chemistry as it is connected to the understanding of the composition, structure and properties of all chemical compounds.

Valence can be defined as the number of bonds a given atom has formed, or can form, with one or more other atoms. For most elements the number of bonds can vary. In fact, the valence number is directly linked to the outermost electron configuration of the atom and, hence, to its position within the periodic table.

Therefore, the elements of the "first group", which have an outermost electronic configuration *ns1* (1 electron in the orbital s of the different shells), can involve in the formation of the bond the only electron they have and are called *univalent* (*monovalent*). It can be said that they have a valence of one and thus can form only one bond.

In the same way, the elements of the "second group" are *divalent* (have a valence of two) because they have two electrons in their outermost shell (*ns2*) which can be involved in the formation of two bonds. And so on so for.

Elements are grouped in the periodic table according with the number of electrons they have in their outermost shell. However, the valence number of an element that matches its group number is not the only one that element can have; in fact this corresponds to its maximum valence.

We have already said that polar covalent and ionic bonds are the most common bonds that can be established between atoms of different elements; that is, bonds where the involved electrons are preferentially attracted by the more electronegative atom or even completely charged on it.

Therefore, chemists decided to numerically express the number of bonds an atom can form by taking into account the above mentioned electrons' delocalization (partial or total), and associating this number (corresponding to the valence) to a sign that can be negative, for the more electronegative atom, and positive for the other.

These are the numbers to which we make reference when using the term "*oxidation number of the element*", assigning to the term "*valence*" the already mentioned meaning (number of bonds).

Oxidation numbers should not be confused with oxidation states. They are usually numerically equivalent, so that these terms are often used interchangeably. In fact, oxidation states indicate the degree of oxidation of an atom in a chemical compound and are represented by integers, which can be positive, negative or zero. On the other hand oxidation numbers are represented by a Roman numeral placed

either as a right superscript to the element symbol, or in parentheses after the name of the element without space between the element and the oxidation number

For example:

✓ NaCl, sodium chloride – ionic bond between Na^+ and Cl^-: the oxidation state of Na is +1 and the oxidation number is I (Na^I) (or, sodium(III). The oxidation number of chlorine is -1 and the oxidation state is I (Cl^I). Both Na and Cl are monovalent.

✓ H2O, water – covalent bonds between hydrogen and oxygen (more electronegative). The oxidation state of H is +1, the oxidation number is H^I, the oxidation state of oxygen is -2 and the oxidation number is O^{II}. Hydrogen is univalent, whereas oxygen is divalent.

1.7 – *Aggregation states of matter*

Depending of ambient pressure, temperature and volume, matter (defined as anything that has both mass and volume, thus occupies space) is commonly said to exist in four states of aggregation, known as phases: solid, liquid, gas and plasma.

For example, let us consider water, which is the only common substance found naturally in all three common aggregation states of matter. At atmospheric pressure, by varying the temperature, water can take both a solid, liquid and gas forms. More precisely at temperatures equal or beneath 0°C (37°F, 273K) water takes a solid form, known as ice. Within a temperature range of 0°C to 100°C it takes a liquid form and above 100°C it converts into a gaseous phase, known as water vapor.

The different states of aggregations of matter are closely related with the different structures that the particles (atoms, ions, molecules) of each substance can mutually have when submitted to different physical conditions and, hence, with the different type of intermolecular bonds that can be formed.

In fact, the atoms, ions, and molecules of *solid phase* materials arrange themselves into tri-dimensional organized structures, occupying regularly distributed equilibrium positions. These ordered structures are known as *crystal lattices*. All solid are characterized by these type of structures that, as a consequence, have their own volumes and shapes.

In comparison with the solid phase, the microscopic particles a *liquid* is made up are close together with no regular arrangement and free to move one another without changing the distance between them. A given liquid has its own volume but assumes the shape of the part of the container which it occupies.

The microscopic particles (in general, molecules) in a *gas phase* are well separated with no regular arrangements and can vibrate and move freely in all directions at high speeds. In the gas phase, particles bounce off the walls of its container, assuming the shape of it.

Finally, in physics and chemistry there exists a particular state of matter, known as *plasma*; it is a state of matter similar to gas in which a certain portion of the gas microscopic particles (molecules or atoms) are ionized (positive and negative ions) through heating or other means, such as strong electromagnetic field applied with a laser of microwave generator. Gas molecular bonds, if present, are in this way dissociated.

There are substances that can apparently resemble solids without being organized into crystalline structures. These substances can be considered as closer to extremely viscous liquids rather than solids. Glasses, and particularly many natural and synthetic substances known as resins or plastics, fall into this category. Often, this pseudo-solid state is identified as "*vitreous state*".

Discussing about water, we have already said that temperature plays a crucial role in the transition from a state of matter to another and, moreover, this transition is related with the type of possible intermolecular bonds of a given substance.

The application of energy, such as temperature, to a solid results in an increase of its thermal state, that is his temperature increases. At a given temperature, the applied energy is strong enough to break some intermolecular bonds, thus allowing molecules to move more freely. The transition form a solid to a liquid phase, called *melting*, starts happening.

A further supply of energy yields exclusively to the breaking of intermolecular bonds present within the solid mass, without an observable increase in temperature. At the completion of the melting process, the substance is converted into a liquid and the temperature starts again increasing till all intermolecular bonds of the substance are completely broken. This is the point to which all molecules start diffusing disorderly in the surrounding atmosphere. The transition from a liquid to a gas phase is called *vaporization*. A schematic representation of all possible phase transitions is shown in figure 1/5.
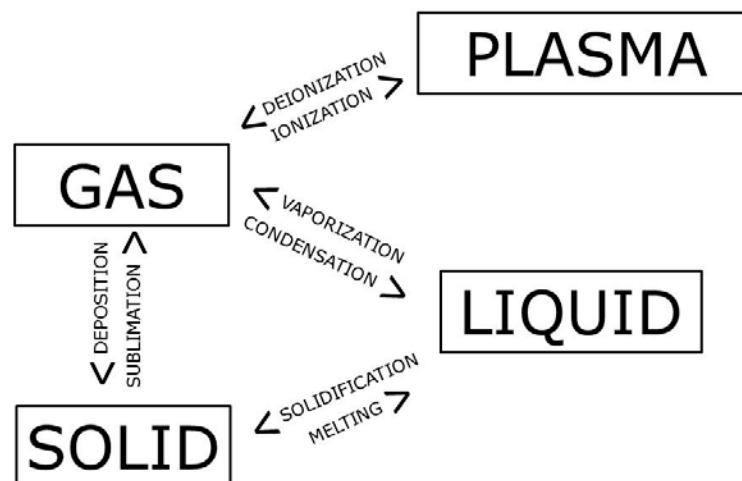

Fig. 1/5 -   Schematic representation of all possible phase transitions of matter

The direct transition from a solid to a gas phase is known as *sublimation*, (common to only few substances), whereas the opposite transition is called *deposition*.

The transition of a given substance from one phase to another happens at well-defined temperature and pressure values. The temperature values at which these

transitions occur are known as *melting point* (and solidification point), *boiling point* (and condensation point), *sublimation point*, etc.

Any pressure variation greatly influences the boiling point of a substance. In fact, the lower the pressure the lower will be the boiling point of a given substance.

However, at atmospheric pressure not all substances can exist in all three common aggregation states of matter. In fact, the temperature needed for some substances to melt or boil could be so high that decomposition (chemical transformations yielding to other simplest substances) phenomena may occur.

Sometimes, but not for all substances, a pressure decrease can be used to lowering the boiling temperature thus allowing the transition from the liquid to the gas phase, without substance's decomposition.

In all phase transitions, what changes is just the state of aggregation of the substance and not its chemical composition; in fact, only the intermolecular bonds are broken, and not the intramolecular ones, so that just a physical and not a chemical transformation occurs.

1.8 – *Heterogeneous mixtures*

Two or more substances, present in the same or different state of aggregations, can be mixed, leading to mixtures that can be both homogeneous or heterogeneous.

Solids, immiscible liquids, liquids and insoluble solids, gases and solids and liquids and insoluble gases can be mixed up to form *heterogeneous mixtures*.

Mixtures of gases, miscible liquids, liquids and soluble solids are called homogeneous mixtures and also known as solutions (already discussed in Part I, chapter 3).

The main heterogeneous systems are reported in table 1/2; in the table the first term represents the dissolved (or dispersed) phase, whereas the second is the continuous medium generally present in higher concentrations.

Solid in solid	Solid mixtures
Solid in liquid	Suspensions (emulsions)
Solid in gas	Smoke, dust
Liquid in solid	Inclusions
Liquid in liquid	Emulsions
Liquid in gas	Aerosols
Gas in solid	Sponges
Gas in liquid	Foams

Tab. 1/2 - Examples of heterogeneous mixtures

1.9 – *Chemical compounds and their nomenclature*

As we have already discussed in paragraph 1.4, atoms can link each other through the formation of chemical bonds. Chemical compounds can be formed by bonding atoms of different chemical elements. Compounds consisting of two chemical

elements are known as *binary compounds*, whereas *tertiary compounds* is the name assigned to those consisting of three elements, and so on.

As has already been said, the bonds of a ionic compound span all over it, whereas pure covalent and polar covalent bonds mainly concern a limited number of atoms which have chemically combined to form a single species known as *molecule*.

Both ionic and covalent compounds can be represented by an expression, known as the *chemical formula*, which states the number and type of atoms present in their molecules. In most cases the chemical formula really corresponds to the compound's molecule; on the contrary, the chemical formulas of ionic compounds conveys just the ratio of elements.

For example, the chemical formula of water (H_2O), states it is a compound consisting of the elements hydrogen and oxygen, which are present in a 2:1 ratio; moreover, as water is a non ionic compound, its formula also expresses the fact that it is really formed by two hydrogen atoms and one oxygen atom.

On the other hand, a molecule of sodium chloride (NaCl) is a ionic compound and its chemical formula states that it consists of just the elements sodium and chlorine present in a 1:1 atomic ratio. The concept of molecule as an elementary unit does not apply to this compound.

Both water (H_2O) and sodium chloride (NaCl) are *individual chemical species*, in the sense that each of them is characterized by a series of chemical and physical properties and, therefore, its own chemical formula.

Thanks to its particular position in the periodic table, the element carbon is able to form unlimited carbon-carbon linear and branched chains, thus allowing the formation of a huge amount of compounds. The huge amount of carbon based compounds and their particular nomenclature, is the subject of a specific branch of chemistry, known as *organic chemistry*. On the other hand, *inorganic chemistry*, which refers to compounds of not-biological origins and not containing carbon-hydrogen bonds, has a simpler nomenclature.

Inorganic compounds will be presented and discussed according with their similar chemical composition characteristics. The most important are the oxides, the hydroxides, the acids and the salts.

1.10 – *Oxides*

Oxides are binary compounds that contain at least one oxygen atom (oxidation state: -2) and one another element (M) in its chemical formula. Depending of the number of bonds (that in turns depends on its oxidation state) a given element can establish with oxygen, more than one oxide can be formed.

The following table 1/3 reports the oxides' general chemical formulas, some examples of oxides and their respective nomenclature.

element's oxidation state	oxide's general formula	examples of oxides	nomenclature
+1	M_2O	Na_2O	sodium oxide
		Cl_2O	dichlorine monoxide
+2	MO	CO	carbon monoxide
+3	M_2O_3	Al_2O_3	aluminium oxide
+4	MO_2	PbO_2	lead dioxide

+5	M$_2$O5	Cl$_2$O$_5$	dichlorine pentoxide
+6	MO$_3$	CrO$_3$	chromium trioxide
+7	M$_2$O$_7$	Cl$_2$O$_7$	dichlorine heptoxide
+8	MO$_4$	OsO$_4$	osmium tetroxide

Tab. 1/3 – Examples of oxides' formulas and relative chemical nomenclature

In addition to the above mentioned nomenclature, the binary compounds that oxygen forms with chemical elements can be distinguished in *oxides* (compounds containing oxygen and chemical elements with a metallic character) and *anhydrides* (compounds containing oxygen and chemical elements with non-metallic character).

Oxides and anhydrides are important compounds in relation to their reaction with water, which yields respectively to the formation of bases and acids.

1.11 – *Acids and bases*

The Arrhenius definition of acids and bases is one of the oldest and states that an acid is a substance that produces hydrogen ions (H$^+$) in aqueous solutions, whereas a base produces hydroxide ions (OH$^-$) in aqueous solutions.

Modern theories define a base as a substance that can donate free electron pairs capable to establish dipolar bonds (also known as dative covalent bond or coordinated bond, a kind of covalent bond in which the two electrons derive from the same atom) with another substance; on the other hand an acid can be defined as an electron pairs acceptor.

As already said oxides and anhydrides react with water to form compounds known as bases and acids consisting of a given element, oxygen and hydrogen.

More precisely, the reaction between a basic oxide and water yields to the formation of a base known as hydroxide, whereas the reaction between an anhydride and water produces an *acid* (sometimes referred to as *oxoacid*, a traditional name for any acid having oxygen in the acidic group; this term stands in contradiction to "*hydracid*", for example hydrochloric acid HCl, lacking oxygen). The chemical formulas of oxoacids are written in a way that hydrogen comes first, then the element and lastly oxygen (e.g. H$_2$SO$_4$, sulphuric acid).

Acids' molecules often contain a number of hydrogen atoms different from that of oxygen. On the other hand, bases' molecules always contain the same number of hydrogen and oxygen atoms and their formulas are written in a way that a certain number of groups OH follow the element (e.g. Ca(OH)$_2$, calcium hydroxide).

In chemistry, the simplest positive integer ratio of atoms of each element present in a compound is known as the *empirical formula* of that chemical compound. On the other hand, the *structural formula* of a chemical compound is a graphical representation of the molecular structure, showing how the atoms are arranged.

To sum up, we can say that for most of the applications of chemistry to restoration:
- ✓ acids are substances that produces hydrogen ions (H$^+$) in aqueous solutions
- ✓ bases are substances that produces hydroxide ions (OH$^-$) in aqueous solutions

✓ hydracids are binary substances consisting of hydrogen bonded to an high electronegative element (e.g. hydrochloric acid, HCl)

1.12 – Measure of acidity – pH

The chemistry of aqueous solutions is dominated by the equilibrium between neutral water molecules and the ions they form.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad (l: \text{liquid } aq: \text{aqueous})$$

Acids and bases produce respectively hydrogen ions (H^+) and hydroxide ions (OH^-) in aqueous solutions: this process is known as dissociation. In a given volume of water, this dissociation can take place to a greater or lesser extent in relation with the acid or base type and quantity.

The abundance of H^+ or OH^- ions divided by the total volume is called *concentration* and is more precisely represented by the: "*number of gram-ions H^+ or OH^- present in 1000 cm^3 (1 litre) of solution*", known as *molar concentration*.

An acid dissolved in water produces a great quantity of H^+ ions so that its concentration is greater than the concentration of OH^- ions. As a consequence the dissolution of a base will produce higher concentration of OH^- ions.

The acidity and basicity of an aqueous solution is measured through a logarithmic value known as pH (pH = -log[H^+], where [H^+] represents the molar concentration of H^+ ion).

pH values can vary from 0 to 14. A solution with pH values ranging from 0 to 7 is defined as acid, whereas values form 7 to 14 identify a basic or alkaline solution. A pH 7 solution is called neutral, as the H^+ and OH^- molar concentrations are equal.

1.13 - Strengths of acids and bases

As we have already seen the pH of an acid or base water solution depends on the molar concentration of H^+ ions. The number of ions produced in a given volume depends not only on the acid or base quantity dissolved in that volume, but mainly on their tendency to release to greater or lesser extent H^+ ions (or OH^- ions).

This tendency is known as strength of acid (or base) and depends on the percentage of acid (or base) that dissociate in water, producing H^+ (or OH^-) ions.

An acid and a base can be schematically represented as H-A and B-OH:

H-A ⇆ H^+ + A^- acid dissociation
B-OH ⇆ B^+ + OH^- base dissociation

The more easily the dissociation reactions happen, that is the more the above mentioned dissociation equilibrium are driven to the right, the higher will be the molar concentration of H^+ and OH^- and, therefore the strength of the acid or the base. Acids that strongly dissociate in water are known as *strong acids*, for example:

HCl   (hydrochloric acid)
HNO_3 (nitric acid)

H_2SO_4 (sulphuric acid)
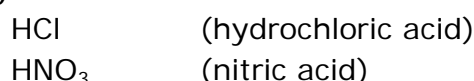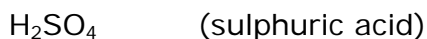
There also exist *medium* and *weak* acids.

Bases that strongly dissociate in water are known as *strong bases* [e.g. NaOH, sodium hydroxide; KOH potassium hydroxide; $Ba(OH)_2$ barium hydroxide], but there also exist *medium* and *weak bases.*

1.14 – *Salts*

The most familiar salt is sodium chloride, NaCl. The neutralization reaction of sodium hydroxide, NaOH, a base, with hydrogen chloride, HCl, an acid, yields to the formation of sodium chloride and water, H_2O:

$$HCl + NaOH \rightarrow NaCl + H_2O$$
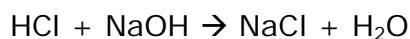
The formula for sodium chloride, NaCl, indicates that equal numbers of sodium and chlorine atoms combine to form the salt. This is called a *normal salt* as it has neither hydrogen (H) nor hydroxyl (OH) in its formula. A salt that has hydrogen in its formula, e.g., sodium bicarbonate ($NaHCO_3$), is called an *acid salt*. A salt that has hydroxyl (OH) in its formula, e.g., copper hydroxyl chloride (Cu[OH]Cl), is called a *basic salt.*

In addition to being classified as normal, acid, or basic, salts are categorized as simple salts (e.g. sodium chloride that contains only one kind of positive ion), double salts [e.g. mineral dolomite , calcium magnesium carbonate, $CaMg(CO_3)_2$, that contains two positive ions], or complex salts (e.g. potassium ferricyanide, $K_3Fe(CN)_6$, that contains a complex ion that does not dissociate in solution).

Moreover, there also exist *hydrates*, which are salts that include water in their solid crystalline form (e.g. mineral mirabilite, hydrous sodium sulphate, $Na_2SO_4\cdot 10H_2O$).

Salts are generally grouped according to the negative ion they contain: carbonates, nitrates, sulphates, chlorides, etc.

1.15 – *Amphoteric behaviour*

Many metals and most metalloids (elements with properties that are in between of those of metals and non-metals) form amphoteric oxides and hydroxides that can react as an acid as well as a base; this property is known as *amphoterism* and depends on the oxidation state of the oxide.

Amphoteric oxides behave as acids or bases depending on the chemical character of the substances with whom they react; in fact, they behave as bases when reacting with acids and as acids when reacting with bases.

As an example, the reaction of aluminium hydroxide, $Al(OH)_3$ with an acid obviously yields to the formation of aluminium salts, whereas in the reaction with a strong base it will behave as an acid, thus forming the correspondent aluminates:

$Al(OH)_3 + 3 HCl \rightarrow AlCl_3 + 3H_2O$ (aluminium chloride) + (water)
$Al(OH)_3 + NaOH \rightarrow Na[Al(OH)_4]$ (sodium tetrahydroxidoaluminate)

1.16 – *Hydrolysis*

Hydrolysis is a chemical reaction of a compound with water resulting in the dissociation into its negative (anion) and positive (cation) constitutive ions.

In the following schematic representation the simplest case of a salt consisting of only one cation and one anion is shown:

$$B^+A^- \rightarrow B^+ + A^-$$

Water, even to a very few extent, also ionizes into negative hydroxyl ions (OH^-) and positive hydrogen ions (H^+):

$$H_2O \leftrightarrows H^+ + OH^-$$
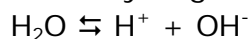
Therefore, a water solution of a salt contains, other than undissociated water, both B^+, A^-, H^+ and OH^- ions.

This salt solution can behave in three possible ways:

a. If the anion A^- and the cation B^+ of a salt belong both to a strong base and a strong acid, they will not have the tendency to bond H^+ and OH^- ions and form undissociated molecules of the acid and the base

b. If the anion of the salt belongs to a strong acid and the cation to a weak or medium-strong base, the cation will have a more or less pronounced tendency to bond the OH^- water anion. Such a tendency can be expressed by writing that the cation reacts with water (hydrolysis) to form undissociated molecules of the base:

$$B^+ + H_2O \rightarrow B\text{-}OH + H^+$$
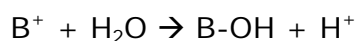
The excess of H^+ ions present in the solution results in the formation of an acid solution (*acidic hydrolysis*)

c. If the anion of the salt belongs to a weak acid and the cation to a strong base, the anion will have a more or less pronounced tendency to bond the OH^- water anion. Such a tendency can be expressed by writing that the anion reacts with water (hydrolysis) to form undissociated molecules of the acid:

$$A^- + H_2O \rightarrow H\text{-}A + OH^-$$
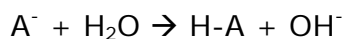
The excess of OH^- ions present in the solution results in the formation of an basic solution (*alkaline hydrolysis*).

An example of behaviour a) is that of sodium chloride, NaCl, which is a salt formed by the reaction between a strong acid (HCl) and a strong base (NaOH):

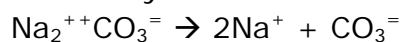$$Na^+ + Cl^- \rightarrow Na^+ + Cl^- \text{ (complete salt dissociation; no hydrolysis; pH=7, neutral solution).}$$
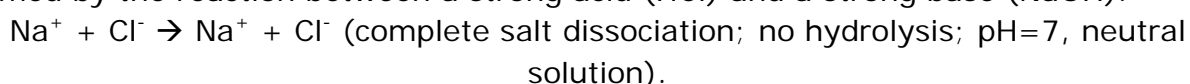
An example of behaviour b) is that of ammonium chloride, NH_4Cl, which is a salt formed by the reaction between a strong acid (HCl) and a weak base (NH_4OH):

$$NH_4^+Cl^- \rightarrow NH_4^+ + Cl^-$$

$$NH_4^{++} + H_2O \rightarrow NH_4OH + H^+ \text{ (acidic hydrolysis; acid solution)}$$
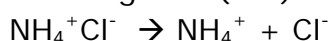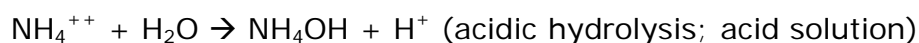
An example of behaviour c) is that of sodium carbonate, Na_2CO_3, which is a salt formed by the reaction between a strong base (NaOH) and a weak acid (H_2CO_3):

$$Na_2^{++}CO_3^= \rightarrow 2Na^+ + CO_3^=$$

$$CO_3^= + 2H_2O \leftrightarrows H_2CO_3 + 2OH^- \text{ (alkaline hydrolysis; alkaline solution)}$$

To sum up we can say that a salt solution can be:

solutions	*salt belonging to*
neutral	strong acid and strong base
acid	strong acid and weak base
alkaline	weak acid and strong base

In the case of salts formed by the reaction between a weak acid and a weak base, the resulting pH will be determined by the relative strength of the acid or the base they belong to.

CHAPTER 2

CHEMICAL REACTIONS

2.1 – *Concept of chemical reaction*

A chemical reaction is a process that lead to the transformation of one set of chemical substances to another.

Unlike phase transitions which involves only intermolecular bonds, a chemical reactions is usually characterized by a chemical change, involving a partial or total breaking of intramolecular bonds and the successive formation of new bonds, hence new products, which usually have properties different from the reactants.

Any chemical substance can be represented by its *structural formula*, which is a graphical representation of the molecular structure, showing the type and number of constitutive atoms, their space arrangement as well as the type of bonds present. This set of structural features (type and number of atoms and bonds) constitute an energy arrangement (chemical energy) characteristic of each particular substance.

More precisely, each constituting atom is characterized by a certain quantity of energy, which results from the equilibrium between its protons, neutrons and electrons; each bond is also characterized by a certain energy that corresponds to energy needed to break it, etc. Therefore, the set of these various forms of energy implies each molecule to possess an overall energy value; in other words any chemical species, at standard environmental conditions, is characterized by a specific fundamental value of total energy.

It is therefore possible to establish an hypothetical scale of chemical energies where each substance occupy a well defined energy level.

Based on this assumption, a chemical reaction can be represented as a process involving the transition of a substance for one energy level to another. The substance (or substances) initially involved in a chemical reaction are called *reactants* (or *reagents*). Reactions often consist of a sequence of individual sub-steps, the so-called elementary reactions, and the information on the precise course of action is part of the reaction mechanism. Chemical reactions are described with *chemical equations*, which graphically illustrate the starting materials, *end products*, and sometimes intermediate products and reaction conditions.

Chemical equations consist of structural formulas of the reactants on the left and those of the products on the right They are separated by an arrow which indicates the direction and type of the reaction: a single arrow ($\rightarrow$) describes a reversible reaction and the tip of the arrow points in the direction in which the reaction proceeds.

A double arrow ($\leftrightarrows$) pointing in opposite directions is used for equilibrium reactions or reversible reactions. In the following schematic representation of a chemical equation, reactants A and B are said to be in equilibrium with products C and D:

$$A + B \leftrightarrows C + D$$
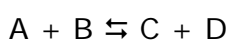
In a chemical reaction, chemical equilibrium is the state in which the concentrations of the reactants ([A] and [B]) and products ([C] and [D]) have not yet changed with time. Usually, this state results when the forward reaction proceeds at the same rate as the reverse reaction and the ratio between the molar concentration of reactants and products remains constant. This process is called dynamic chemical equilibrium and is expressed by a constant:

$$K_{eq} = \frac{[C] \cdot [D]}{[A] \cdot [B]}$$

The value of the equilibrium constant (K_{eq}) varies depending on external physical conditions such as temperature and pressure and, as a consequence, the single molar concentrations of the involved substances vary accordingly. Therefore, it may happen that under certain conditions the molar concentrations of the products can be higher than those of the reactants and vice versa, under other conditions. This means that are the external conditions under which a reaction takes place that control whether the forward reaction, instead of the reverse reaction, should preferentially take place.

2.2 – *Exothermic and endothermic reactions*

For a substance to be transformed into another, it is first of all necessary to break the intramolecular bonds constituting its molecule. This process often requires the supply to the reactant (or reactants) of a certain energy (ΔE) known as *activation energy*.

Therefore, some energy should be supplied to the reactant (A) in order to move it at least at an activated state (B). The second reaction stage foresees the establishment of new bonds and an higher or lower than the energy initially supplied to the reactant will be released.

An endothermic reaction is a chemical reaction that is accompanied by the absorption of energy. In other words, the energy needed for the reaction to occur (ΔE_{AB}) is higher than the total energy released (ΔE_{BC}). As a result of this, the reaction need extra energy (ΔE_{CA}) to be performed (usually in the form of heat) (Fig. 2/1).
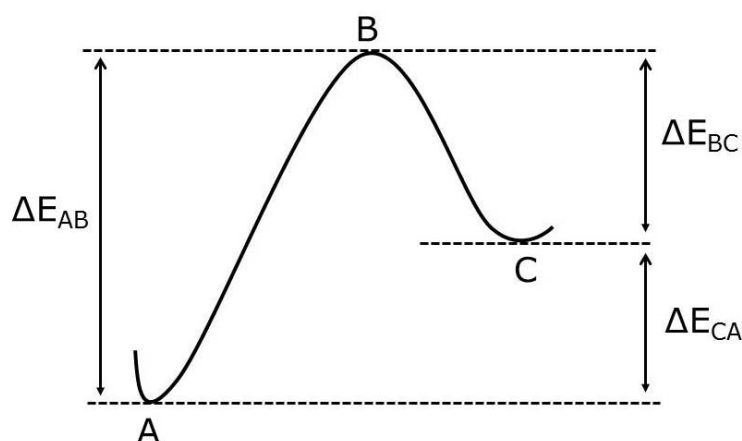
An exothermic reaction is a chemical reaction that is accompanied by the release of heat. In other words, the energy needed for the reaction to occur (ΔE_{AB}) is less than the total energy released (ΔE_{BC}). As a result of this, the extra energy (ΔE_{CA}) is released, usually in the form of heat.
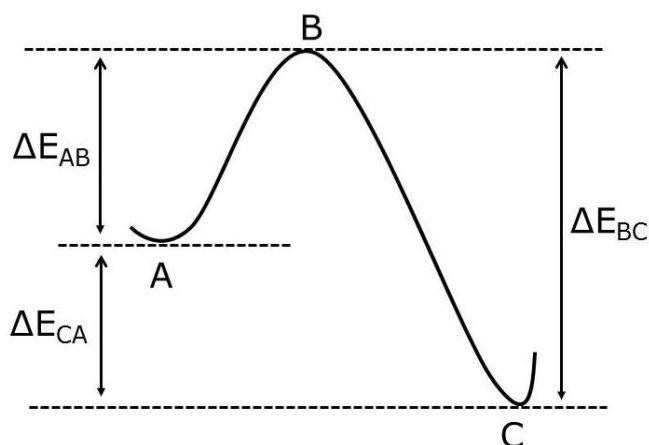

Fig. 2/2 – An energy profile of an exothermic reaction

Not always the reaction performance is favoured by the supplying of heat. In fact, while endothermic reactions (the system absorbs energy) are favoured by the supply of heating (the reaction proceeds towards the products' formation), exothermic reactions are unfavourable to such an heating supply.

2.3 – *Catalysis*

Depending on the nature of the reactants and the experimental conditions, chemical reactions reach an equilibrium in a short or large period of time.

Under normal experimental conditions, each chemical reaction happens at a certain *reaction rate*. A temperature increase raises the rate of a chemical reaction. However, a reaction rate increase can also be achieved by the participation of substances called *catalysts*. This process is known as *catalysis*. Catalysts are added in very few quantities, are not consumed by the reaction itself and are aimed at facilitating the breaking of chemical bond and lowering the *activation energy* (E_a), that is the energy that must be overcome in order for a chemical reaction to occur. The effect of a catalyst in a hypothetical exothermic chemical reaction involving reactants A and B to give C, is shown in figure 2.3.
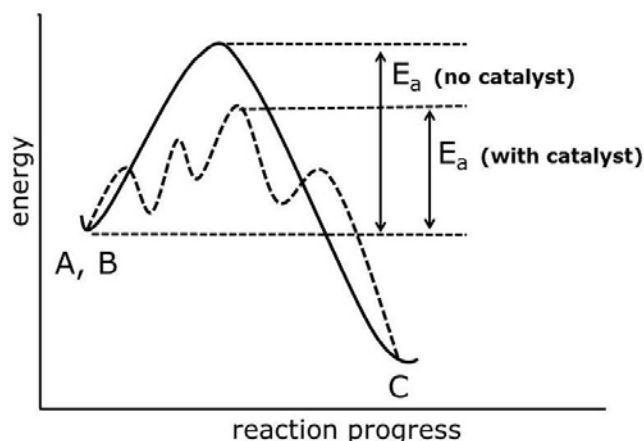
Fig. 2/3 – Schematic drawing showing the effect of a catalyst in an hypothetical exothermic reaction A + B to give C. The addition of a catalyst lowers the activation energy (E_a) (dotted line) that must be overcome in order to produce C.

Very often catalysts consist of solid substances in a powder form which held increasing their active surface.

As an example, catalytic reactions involving the addition or subtraction of hydrogen form a molecule and performed in the presence of platinum powder, are very common in chemistry.

In the field of biology, almost all chemical reactions may occur at lower temperatures thanks to the catalytic action played by particular substances known as enzymes (see, part I, chapter 3, paragraph 3.11).

Substances that slow a catalyst's effect in a chemical reaction are called *inhibitors*, which are sometimes referred to as "*negative catalysts*" since they decrease the reaction rate. As an example, commercially available hydrogen peroxide is sold with the addition of few quantities of negative catalysts, which are added to avoid its easy decomposition.

2.4 – *Type of chemical reactions*

Many are the type of chemical reactions involving inorganic compounds; the most important are:

a- Synthesis reactions
b- Addition reactions
c- Decomposition reactions
d- Single displacement (or substitution) reactions or double displacement reactions
e- Oxidation-reduction (or redox) reactions

In a *synthesis reaction* two or more chemical species combine to form a more complex product: (A + B → AB).

In *addition reactions* reactants sum each other and at least one of the reactants is a compound.

Decomposition reactions can be considered the inverse of synthesis and addition reactions. In fact, in a decomposition reaction a compound is broken into smaller chemical species (AB → A + B).

A substitution or *single displacement reaction* is characterized by one element being displaced from a compound by another element (A + BC → AC + B), whereas in a *double displacement reaction* two compounds exchange bonds or ions in order to form different compounds (AB + CD → AD + CB). An example of a double displacement reaction occurs between two soluble salts; among this type of reactions are of the outmost importance those yielding to an insoluble salt that is subtracted from the equilibrium in the form of a "*precipitate*".

An *acid-base reaction* is a type of *double displacement reaction* that occurs between an acid and a base. The H^+ ion in the acid reacts with the OH^- ion in the base to form water and an ionic salt ($HA_{(acid)}$ + $BOH_{(base)}$ → H_2O + $BA_{(salt)}$).
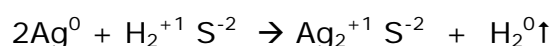
In a *redox reaction* the oxidation numbers of atoms are changed. Redox reactions may involve the transfer of electrons between chemical species. In details, the oxidation number/state of any free element (uncombined element) is zero; when atoms form compounds, they lose, gain or put in common electrons to establish chemical bonds, thus their oxidation number changes in respect to the uncombined situation.

In a redox reaction *oxidation* is the loss of electrons or an *increase* in oxidation state by a molecule, atom, or ion; on the other hand, *reduction* is the gain of electrons or a *decrease* in oxidation state by a molecule, atom, or ion.

$$\overbrace{A_{ox} + B_{red}}^{reduction} = A_{red} + \underbrace{B_{ox}}_{oxidation}$$
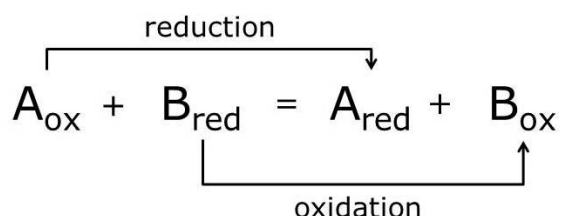
To sum up, substances that have the ability to oxidize other substances are said to be oxidative or oxidizing and are known as *oxidizing agents*, oxidants, or oxidizers. In other words, the oxidant (oxidizing agent) (A_{ox}) removes electrons from another substance; i.e., it oxidizes other substances, and is thus itself reduced (A_{red}).

As an example, the tarnishing of silver upon exposure to air, containing hydrogen sulphide, yields to the formation of silver sulphide and gaseous hydrogen:

$$2Ag^0 + H_2^{+1}S^{-2} \rightarrow Ag_2^{+1}S^{-2} + H_2^0\uparrow$$

If we consider the oxidation states of the atoms involved in the redox reaction, we can notice that the oxidation number of sulphur (-2) in unchanged, whereas that of silver has changed from 0 to +1 and that of hydrogen from +1 to 0. In this case, silver has lost one electron and is thus oxidized, whereas hydrogen has gained one electron and is thus reduced.

BASIC OF ORGANIC CHEMISTRY
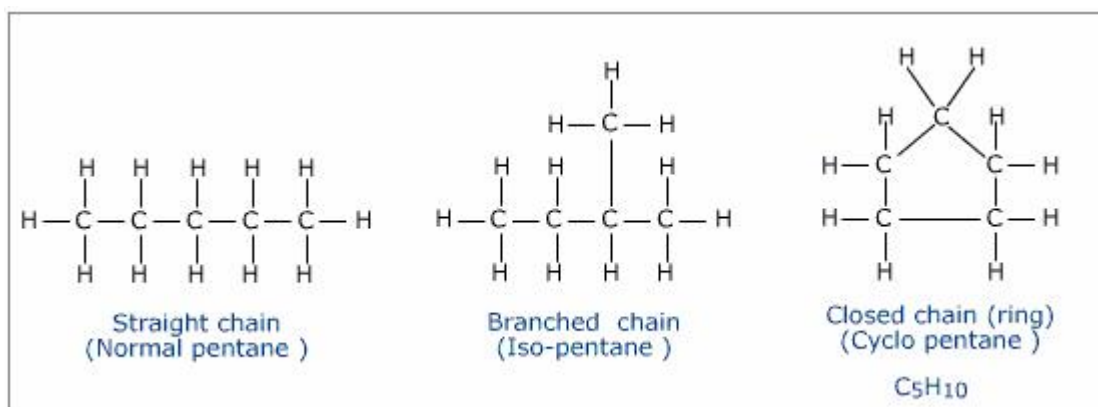

3.1 – *Organic compounds*

We have already mentioned the possibility of carbon to form a large number of compounds, thanks to its ability to form long-chain hydrocarbons. The carbon's valence number is always four, so that it can establish with other atoms four bonds.

Carbon atoms can establish between them covalent bonds in different ways:

single bond

double bond

triple bond
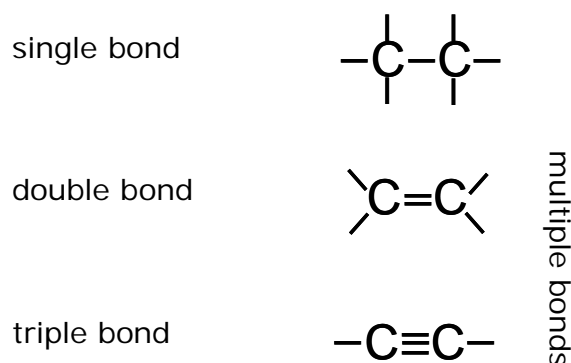
multiple bonds

Not necessarily a compound contains only single, double or triple bonds, but they can be present at the same time within the molecule. In general, the most present bond is the single bond.

If we also include the different type of carbon-carbon bonds, a huge amount of molecules and respective compounds, characterized by *open* or *closed*, *linear* (*straight*) or *branched* long chains hydrocarbons, can be obtained. Moreover, the substitution of an hydrogen atom with functional groups (consisting of different group of atoms), opens up the possibility to obtain an even larger number of organic compounds. To sum up, most carbon-containing compounds are organic, and most compounds with a C-H bond are organic.

Straight chain
(Normal pentane)

Branched chain
(Iso-pentane)

Closed chain (ring)
(Cyclo pentane)

C_5H_{10}

3.2 – *Classification of organic compounds*

Organic chemistry is the science concerned with all aspects of organic compounds that either form the basis of, or are important constituents of, many products including plastics, drugs, petrochemicals, food, textiles, dyes, detergents, solvents, adhesives, varnishes, and paints. They form the basis of almost all earthly life processes.

The simplest organic compounds consists of molecules containing, other than carbon, only hydrogen. These compounds are knows as *hydrocarbons.*

Methane is the simplest hydrocarbon, consisting of one single carbon atom bonding four hydrogen atoms that saturate its valence number of 4.

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$$
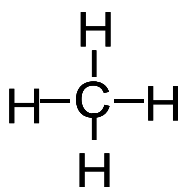
methane

Organic compounds are classified into series according to the *type of chain* formed by carbon atoms and the *type of bonds.*

Hydrocarbons are subdivided into three groups:

1st Group – *Aliphatic hydrocarbons*, that are characterized by open chains (linear or branched), and are subdivided into three groups according to their state of saturation (type of carbon-carbon bond):

  a) Saturated aliphatic hydrocarbons, or *paraffins* or alkanes: only single C-C bonds present;
  b) Unsaturated aliphatic hydrocarbons, or *olefins* or alkenes: one or more double C=C bond present;
  c) Unsaturated aliphatic hydrocarbons, or *acetylenes* or alkynes: one or more triple C ≡ C bond present.

The term unsaturated is used when any carbon structure contains double or occasionally triple bonds.

The already mentioned methane (CH_4) is the simplest saturated hydrocarbon.

Ethylene ($CH_2=CH_2$) is the simplest unsaturated hydrocarbon and consists of two carbon atoms bonded together by a double bond, whereas the organic compound characterized by the presence of two carbon atoms bonded together by a triple bond, is known as acetylene (H-C ≡ C-H).

2nd Group – Alicyclic hydrocarbons

An alicyclic compound is an organic compound that is both aliphatic and cyclic. They contain one or more all-carbon rings and may or may not have aliphatic side chains attached:

a) Saturated alicyclic hydrocarbons or cycloparaffins: presence of only single bonds

b) Unsaturated alicyclic hydrocarbons: presence of at least one multiple bond (double or triple).

3rd Group – Aromatic hydrocarbons

Aromatic hydrocarbons are a particular type of unsaturated cyclic hydrocarbons, possessing properties which are very different from normal unsaturated hydrocarbons. Aromatic hydrocarbons manifest a cyclic delocalization of bonding electrons. This is usually considered to be because electrons are free to cycle around circular arrangements of atoms (in general six-membered carbon ring) that are alternately single- and double-bonded to one another. The most important example is *benzene*, which is composed of 6 carbon atoms in a ring, with 1 hydrogen atom attached to each carbon atom, with the molecular formula C_6H_6.

A benzene molecule can be represented in various ways:
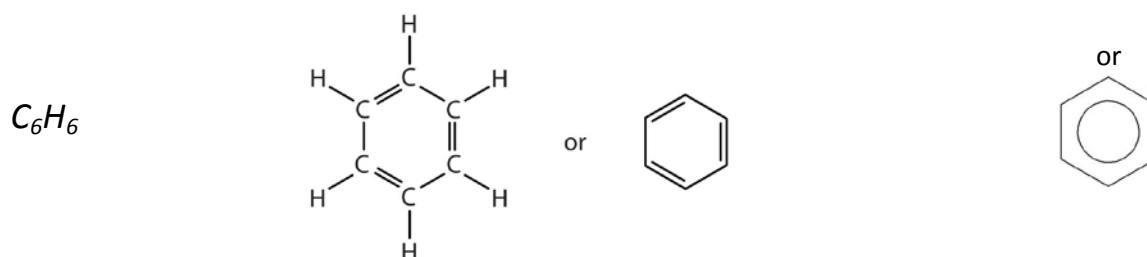
3.3 – *Hydrocarbons, nomenclature and properties*

The International Union of Pure and Applied Chemistry (IUPAC) created and developed a set of rules to generate systematic names of both inorganic and organic chemical compounds. To use the systematic naming, one must know the structures and names of the parent structures.

Apart from the common names given to the first paraffinic compounds, the other hydrocarbons are named according to the number of carbon atoms contained in their molecules:

CH_4		methane	
$CH_3 - CH_3$	C_2H_6	ethane	
$CH_3 - CH_2 - CH_3$	C_3H_8	propane	
$CH_3 - CH_2 - CH_2 - CH_3$	C_4H_{10}	butane	
$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$	C_5H_{12}	*pent*-ane	Greek, pente = 5
	C_6H_{14}	*hex*-ane	Greek, eksi = 6
	C_7H_{16}	*hept*-ane	Greek, epta = 7

Paraffinic, olefins and acetylene compounds are named by adding respectively to the Greek number, corresponding to the number of carbon atoms, the suffix *ane*, *ene* and *yne*.

1   2   3   4

CH$_3$ – CH = CH – CH$_3$ 2-but-*ene*   (2 indicates the position of the double bond within the molecule)

1   2   3   4   5

CH$_2$ = CH – CH$_2$ – CH$_2$ - CH$_3$ 1-pent-*ene*

1   2   3   4   5

CH$_3$ – C ≡ C – CH$_2$ – CH$_3$ 2-pent-*yne*

The first four saturated aliphatic hydrocarbons are gases, whereas the members containing 5 up to 15 carbon atoms are liquids and those above 15 are solids.

In comparison with saturated hydrocarbons, unsaturated hydrocarbons are more reactive. In fact, the unsaturations (double, triple bonds), present within their molecules, represent preferential reaction places. Alicyclic hydrocarbons behave in the same way.

Aromatic hydrocarbons are scarcely reactive as the "aromatic bond", being delocalized within the entire molecule, confers a certain stability and does not allow an easy localization of preferential reaction places.

Liquid aromatic hydrocarbons are frequently used as solvents in the field of restoration.
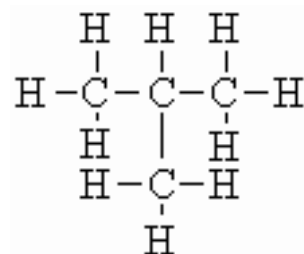
3.4 – *Isomerism*

Unlike inorganic compounds which are clearly identifiable through their single molecular formula, organic compounds are subjected to *isomerism*. In fact, *isomers* are compounds with the same molecular formula but different structural formulas (showing how the atoms are arranged).

As an example the molecular formula of butane C$_4$H$_{10}$ may refer to either of the two structural isomers *n*-butane and isobutane:
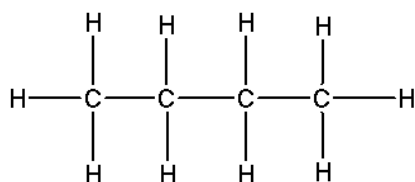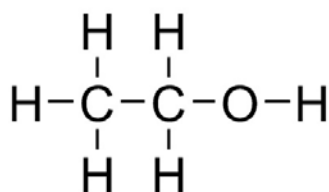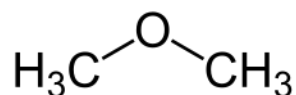

normal butane (*n*-butane)   isobutane (or methylpropane)

and, the molecular formula C$_2$H$_6$O may refer to either of the two structural isomers ethyl alcohol and methyl ether:

ethyl alcohol (CH_2CH_2OH)   methyl ether (CH_3OCH_3)

3.5 – *Halogenated hydrocarbons*

Halogenated hydrocarbons are a group of organic compounds derived from hydrocarbons containing one or more halogens (F, Cl, Br, I) substituting hydrogen atoms within the molecules.

The more common are the chlorinated hydrocarbons derived from methane:

CH_3Cl	chloromethane or methyl chloride
CH_2Cl_2	dichloromethane or methylene chloride
$CHCl_3$	trichloromethane or chloroform
CCl_4	tetrachloromethane or carbon tetrachloride

The following compounds derive from ethylene:

$Cl_2C = CCl_2$	tetrachloroethylene
$CHCl = CCl_2$	trichloroethylene (marketed in Italy as "*trielina*")

Halogenated hydrocarbons are quite reactive substances and are often used for the preparation of many other organic compounds.

Some of them are toxic and irritating, some others are used as insecticides and fungicides. Many of them have been used as a solvent for fats, oils, waxes, resins, rubber, plastics, paints, and varnishes. By 1990 their use was banned in many states.

3.6 – *Alcohols*

Alcohols are organic compounds in which the hydroxyl functional group (-OH), substituting an hydrogen atom, is bound to a carbon atom.

Alcohols are classified into *primary*, *secondary*, and *tertiary*, based upon the number of carbon atoms connected to the carbon atom that bears the hydroxyl group.
Examples of primary alcohols are :

CH_3–OH	methanol or methyl alcohol
$CH_3 –CH_2 – OH$	ethanol or ethyl alcohol
$CH_3 –CH_2 – CH_2 – OH$	propan-1-ol or n-propanol, propyl alcohol
$CH_3 –CH(OH) – CH_3$	propan-2-ol or 2-propanol, isopropyl alcohol

The last two alcohols are isomers as they have the same molecular formula C_3H_7OH but the hydroxyl functional group is located within the molecule respectively on the carbon atom number 1 and number 2.

In the IUPAC nomenclature the name of the alkane chain loses the terminal "*e*" and adds "*ol*", e.g., "methanol" and "ethanol". When necessary, the position of the hydroxyl group is indicated by a number between the alkane name and the "*ol*", e.g., propan-1-ol and propan-2-ol.

Polyols are alcohols containing multiple hydroxyl groups. A molecule with two hydroxyl groups is a *diol*, one with three is a *triol*, one with four is a *tetrol* and so on.

The chemical and physical properties of alcohols result from the number of carbon atoms, the chain structure (linear or branched) and the number of hydroxyl groups present in their molecules.

Methanol, ethanol, and propanol are miscible in water, whereas butanol, with a four-carbon chain, is moderately soluble. Alcohols from five up to eleven carbons (pentanol and higher) are viscous liquids, effectively insoluble in water. Higher alcohols are solids. All simple alcohols are miscible in organic solvents and, especially ethanol, is used as solvent.

3.7 – *Ethers*

Ethers are a class of organic compounds that contain an oxygen atom connected to two alkyl or aryl radicals. In organic chemistry any hydrocarbon that had lost one or more hydrogen atoms is called a radical and is represented as –R. As an example:

CH$_4$ methane   → -CH$_3$ methyl radical
CH$_3$-CH$_3$ ethane   → -CH$_2$-CH$_3$ ethyl radical
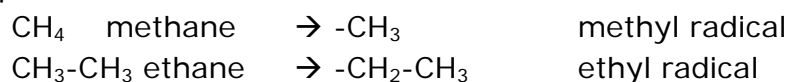
The general formula of ethers can be represented as R-O-R′; the two –R radicals can be identical or different. The most common ethers are:

CH$_3$–O–CH$_3$ *dimethyl ether*

CH$_3$–CH$_2$–O–CH$_2$–CH$_3$ or (C$_2$H$_5$–O–C$_2$H$_5$)   *diethyl ether*, commonly referred to as simply *ether*, but was once called sulphuric ether and *sweet oil of vitriol*.

Ethers and diethyl ether in particular are used as solvents for many substances. Moreover, aliphatic ethers in particular are scarcely reactive and can be used as solvents in chemical reactions performed in solution.

In general, they are poorly soluble in water, but miscible with the majority of organic solvents.

3.8 – Aldehydes and ketones

Aldehydes and ketones are two classes of organic compounds that contain a carbonyl group C=O (a carbon-oxygen double bond).

In aldehydes, the carbonyl group has a hydrogen atom attached to it, together with either a second hydrogen atom or, more commonly, an hydrocarbon radical –R.

In ketones, the carbonyl group has two hydrocarbon radicals attached.
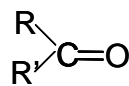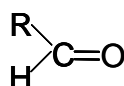
aldehyde   ketone

Aldehydes and ketones have almost the same chemical properties because they both have a carbonyl group in their molecules; ketones are just more resistant to oxidation as they do not have an hydrogen atom attached to the carbonyl group.

3.9 – Carboxylic acids

Carboxylic acids are a class of organic compounds that contain the carboxyl group (or carboxy): –COOH. The general formula of a carboxylic acid is R-COOH:

$$R-C\begin{matrix} O-H \\ \\\\ O \end{matrix}$$
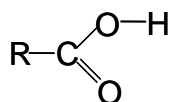
carboxylic acid

Acids with two or more carboxyl groups are called dicarboxylic, tricarboxylic, etc. The simplest carboxylic acids are:

$H-COOH$	formic acid or methanoic acid
CH_3-COOH	acetic acid or ethanoic acid
CH_3-CH_2-COOH	propionic acid or propanoic acid
$(COOH)_2$	oxalic acid or ethandioic acid

In the IUPAC nomenclature of carboxylic acids the name of the correspondent hydrocarbon loses the terminal "*e*" and adds "*oic*", e.g., "methanoic" acid.

The main property of the functional group –COOH is that it undergoes a partial dissolution in water, yielding to $-COO^-$ and H^+ ions.

This explains their acidity and the possibility to react with bases to form organic salts, among which the most known are acetates $CH3-COO^-$.

Carboxylic acids characterized by short aliphatic chain, thus the effect of the carboxyl group predominates, are liquid, water soluble and show medium acidic properties. The higher the molecular weight of the acid, thus the longer the hydrocarbon chain, the lower are the acidic properties and water solubility and the higher the melting and boiling temperatures.

Saturated monocarboxylic acids characterized by long-chain hydrocarbon are solids, resembling paraffins and are called fatty acids, such as palmitic and stearic acid. The presence of unsaturations in the hydrocarbon chain, lower down the melting point of carboxylic acids (oleic acid, linoleic acid, linolenic acid, etc.).

In fact, in this case the properties deriving from the presence of the carboxyl group are very limited if compared with those deriving from the hydrocarbon chain; this results in a substance much similar to a common high molecular weight hydrocarbon. After all, this is true for all classes of hydrocarbons.

Carboxylic acids are used for the preparation of many other organic substances, such as esters.
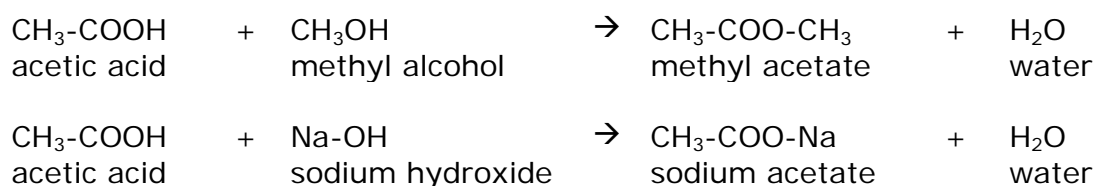
3.10 – Esters

Esters are a class of organic compounds in which at least one -OH (hydroxyl) group is replaced by an -O-alkyl (alkoxy) group. The general formula of an ester is R-COOR':

$$\begin{array}{c} O \\ \parallel \\ C \\ R \quad\quad OR' \end{array}$$
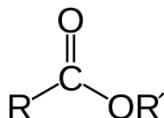
chemical formula of esters

Esters are most commonly formed by condensation reactions between carboxylic acids and alcohols in the same way as in inorganic chemistry a salt is obtained from the reaction between an acid and an hydroxide.

Their nomenclature also recalls the one used for inorganic salts:

| $CH_3\text{-}COOH$ | + | CH_3OH | → | $CH_3\text{-}COO\text{-}CH_3$ | + | H_2O |
| acetic acid | | methyl alcohol | | methyl acetate | | water |

| $CH_3\text{-}COOH$ | + | Na-OH | → | $CH_3\text{-}COO\text{-}Na$ | + | H_2O |
| acetic acid | | sodium hydroxide | | sodium acetate | | water |

Esters are substances widely diffused in nature. Some flowers' and fruits' essences are made of esters.

Most naturally occurring fats, oils and waxes are esters as well as while polyesters are important plastics, with monomers linked by ester moieties.

Liquid esters, primarily acetates, can be used as solvents.

3.11 – *Amines*

Amines are organic compounds that contain a basic nitrogen atom with a lone pair. Amines derive from ammonia (NH_3), wherein one or more hydrogen atoms have been replaced by a substituent (-R) such as an alkyl or aryl group.

Therefore, amines can exist as primary ($R\text{-}NH_2$), secondary ($R_2\text{-}NH$) and tertiary ($R_3\text{-}N$) amines depending of the number of replaced hydrogen atoms.

Amines with a low number of carbon atoms are gaseous; an increase in their molecular weight turn them into liquid substances, whereas at higher molecular weights they are solid. Solubility decreases with the increase in the number of carbon atoms.

Like ammonia, amines are bases, in some cases even stronger than ammonia itself; the nitrogen atom features a lone pair that can bind a H^+ ion to form an ammonium ion R_3NH^+.

From an industrial point of view, aliphatic amines are less important than aromatic ones, among which the simpler term is aniline (or phenylamine).

Some aliphatic amines, such as *n*-buthylamine, were extensively used in past restoration interventions.

3.12 – *Macromolecules – The polymerization*

Unlike inorganic substances, many organic substances can form *macromolecules*, which are very large molecules commonly produced by *polymerization* of smaller (consisting of few atoms) subunits. The individual constituent molecules of macromolecules are called *monomers* and the formed macromolecules are known as *polymers* or *resins*.

A polymerization reaction can be represented as follows:

nM   →   .........M-M-M-M.....M-M.....

monomer   polymer

n=number of monomer units, M=single monomer unit

Polymerization reactions completely modify the chemical and physical properties of the starting monomers and it can be in general said that there exist more similarities between different polymers obtained from the different type of monomers, than between a given polymer and its starting monomer.

Polymerization reaction are very common in nature; as an example we can make reference to some of the most widely diffused natural polymers such as cellulose and starch constituting plants, proteins constituting leaving organisms or natural rubber (caoutchouc).

Especially after the second world war the chemical industry has been able to synthesize for many common and more specific purposes, a very large number of synthetic polymers, often known as "plastics". Research and development in polymer chemistry is still very active and expanding.

Macromolecules possess chemical, chemical-physical and physical properties different from molecules of shorter dimensions.

The most important properties are:

a) molecular weight

The molecular weight of a polymer is obviously very high if compared with that of a normal molecule. The result of a polymerization reaction is always the formation of substances composed of macromolecules with similar, but exactly the same, molecular weights. In fact, the probability that all monomers involved in polymerization reactions yield to the production of polymer chains or three-dimensional structures of the same type, is very unfavourable.

b) physical structure of polymeric materials

Solid materials, consisting of atoms, ions and simple molecules are structured into simple units organized into three-dimensional ordered networks having a characteristic geometrical shapes and dimensions.

On the contrary, most of polymers have amorphous, vitreous structures, even though there are exceptions.

c) chemical properties

Briefly, we can say that polymers may contain specific atoms or groups of atoms that modify the chemical properties of their basic chain structure. In general, polymers are chemically inert materials as there are not easily affected by acids, bases, oxidants and organic reagents.

d) chemical-physical properties

- *solubility*: only thermoplastic resins show a certain solubility; in fact, thermosetting resins, due to their three-dimensional and cross-linked structure are almost insoluble and the action of solvent is limited to swelling phenomena induced by the absorption of the solvent within the polymer structure.

  Thermoplastic resins consisting of distinct molecules, even though of high molecular weight and long chain hydrocarbons, can be dispersed into a solvent following a mechanism similar to that of a liquid into liquid dispersion. In the reality, these polymer "solutions" consist of fine micro aggregates dispersions (micelles) of molecules, commonly known as *colloidal dispersions.*

- *adhesion, cohesion and film-forming properties*

  Cohesion can be defined as the set of attractive intermolecular forces of like molecules, that is the interactions sticking together the molecules constituting a substance.

  On the other hand, adhesion is the tendency of dissimilar molecules (hence substances) to cling to one another.

  Depending on the reciprocal adhesion and cohesion values, many polymers can show film-forming properties when applied in solution (or dispersion) onto a surface.

- *mechanical properties*

  Elasticity and *plasticity* are the most important mechanical properties of polymers. Any solid material submitted to stress, undergoes deformations which are directly linked to its structure and intermolecular forces that make its molecules sticking to one another. These deformations can be either reversible or irreversible. *Plasticity* is the propensity of a material to undergo permanent deformation under stress, whereas elasticity refer to Materials that deform reversibly under stress.