





The States-Of-Matter Approach to Introductory Chemistry (SOMA)

This is an introductory chemistry course for upper secondary chemistry (grade 10) (chemistry for general education). The course introduces chemistry is a logical and at the same time pedagogically sound way, by means of the three states of matter. The course consists of three majors units and is intended for 3 periods per week course. The units are:

- A. Air, Gases, and the Gaseous State
- B. Salt, Salts, and the Solid State
- C. Water, Liquids, and the Liquid State

In gases, the molecules are small, only a few non-metals (O, H, N, C, S, F, CI, and inert gases) are studied. Covalent bonding only enters. No intermolecular interactions exist. The study of hydrocarbons provides for an integrated study of inorganic and organic chemistry. Atomic and molecular structure (but not the periodic table) is introduced here. Chemical reactions, stoichiometry, reaction energetics, and gas laws provide the physical chemistry part of the unit.

- In salts, ionic bonding and crystal structure are studied. The periodic table and oxidation number are introduced here. Covalent solids and metals are also part of the unit.
- In liquids, intermolecular bonds are treated. Organic chemistry is part of the unit. Solution chemistry and acids and bases (including organic acids) are studied here. The unit concludes with chemical reaction sin aqueous solutions.
- Each major unit includes a corresponding major social and environmental issue. Air pollution, the green house effect, and the depletion of ozone layer are a major theme in air and gases. Waste disposal, and recycling of materials (especially of metals) are considered with solids. Water quality, water pollution, and acid rain are themes in water and liquids.

A relevant book has been written in Greek as part of the M.Sc. thesis in chemistry education by E. Pyrgas under the supervision of G. Tsaparlis. From this book are the following pages that start Part B. Translation into English is by Georgios Tsaparlis.

Reference:

Tsaparlis, G. (2000). The **S**tates-**O**f-**M**atter **A**pproach to Introductory Chemistry (SOMA). *Chemistry Education Research and Practice*, 1, 161-168.

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| Ν | |
| | |
| Т | salt, |
| | salts, |
| В | and the solid state |

- **B 1** salt and the crystal structure **B 2** salts, metal oxides, and
- metal hydroxides **B** 3 molecular solids
- **B4** metals
- **B 5** solid waste and its management

B1 SALT AND CRYSTAL STRUCTURE

B 1.1 Cooking salt

Our familiar cooking salt is the chemical compound **sodium chloride**, NaCl.

A large amount (~3.5% w/w) of sodium chloride is dissolved in sea water, and this causes the salty taste of sea water. Sea water also contains dissolved smaller quantities of other salts (e.g. salts of bromine and of magnesium). Salt is obtained from salt sea lakes (swallow areas in sea gulfs). Because of the small depth, water evaporates during summer, and slat and the other dissolved salts remain. From this natural salt, we obtain pure salt by means of *re-crystallisation* (see below).

Salt forms extended levels of deposits (**mineral salt**) in many parts of the earth, and in dried lakes and seas. Mineral salt constitutes the main mineral for the element sodium. From salt mines, salt is extracted by means of digging-out (*mining*) or by passing of hot water (in which salt has large solubility) and sucking of the salt solution.

A very small quantity (~50 ppm) of potassium iodide (KI) is added to cooking salt to provide protection to the thyroid gland. This is *iodided salt*. On the other hand, because salt in the human body contributes to increased blood pressure, people who have increased blood pressure should reduce salt consumption with their food. To this purpose, salt with reduced content in NaCI is commercially available. It contains potassium chloride (KCI) as substitute for salt, in quantities 25% and even 50% w/w.

Except for cooking, salt is used as food preservative, for the preparation of sodium, baking soda, industrial soda, and other industrially important compounds.

Crystallisation and re-crystallisation

If we take sea water and boil it in a pan, all liquid water will transfer to the gas phase, leaving a white powder on the bottom of the pan. This powder is nothing else than various substances (mainly salt, mainly NaCl) that were dissolved in the sea water. This phenomenon is crystallization. It can occur of its own by leaving sea water to stay for a long time in an open pan. Note that solid crystals will start forming in the process of boiling or evaporation, that is, well before the whole water evaporates.

Sometimes, crystals are not poor, but contain various admixtures, e.g. soil (like dry salt that is collected from salt mines). This is due to the complete removal (evaporation of water, leaving behind the mixture of substances that were contained in solution. We can take pure crystals by dissolving the substance in de-ionised water, and then by allowing the substance to crystallise, without letting all the solvent (the water) evaporate. This process is called **re-crystallisation**. Re-crystallisation is a very useful process for chemistry, allowing the preparation of pure substances.

Minerals are homogeneous solid components of the solid earth shell that have unique *crystal structure* and *chemical composition*. The later is characterised by a specific *chemical formula*.

NaCl is an electrolyte

In solid state, NaCl is not a conductor of electricity. But when it is melted or when it is dissolved into water, it conducts electricity (Fig. 1). On passing of the electric current through melted NaCl, the phenomenon of electrolysis takes place. In the two electrodes, the constituent elements of sodium chloride are liberated: metallic sodium on the negative electrode (cathode), and chlorine gas on the positive electrode (anode).



Fig. 1 On melting, the sodium chloride crystals 'break', when the ions move about freely. This explains why melted NaCl conducts electricity.

B 1.2 Ionic or heteropolar bond

The electric conductivity of melted NaCl and of the NaCl aqueous solution is due to the same reason: the structural units of NaCl are electrically charged particles, called ions.

The sodium atom (Z = 11) has one valence electron, which it holds loosely: sodium has small electronegativity, it is an electropositive element. For this reason, the single valence can easily be detached/removed from the electrically neutral atom. In this way the *electrically neutral* sodium atom becomes the *positively-charged sodium ion* (cation):

 Na^+ has the same valence structure as its predecessor in atomic number atom of the inert gas neon (Ne. Z = 10), with 8 valence electrons.

The electronic theory of valence

The same year that G.N. Lewis explained covalent bond in non-polar, homonuclear molecules (e.g. H_2), S. Kossel proposed the electronic theory of valence. This theory explained the formation of stable ions, due to the tendency of atoms to gain or give out electrons so that to acquire the inert-gas valence structure.

On the contrary, the chlorine atom (Z = 17) has 7 valence electrons, so easily can take up one more electron, acquiring in this way the valence structure of the atom of next in atomic number element, the inert gas argon (Ar, Z = 18). In this way the *electrically neutral chlorine atom* becomes the *negativelycharged chloride ion* (**anion**):

$$Cl_2 + 2e^- \rightarrow 2 Cl^-$$

During electrolysis, *cations* move to the *negatively charged electrode* (**cathode**), while *anions* move to the *positively charged electrode* (**anode**).

Because of the electric charge, ions do not exist isolated in nature. Cations can co-exist only with anions, in which case each cation attracts neighboring anions and repels neighboring cations, and vice versa. These forces have as result the holding together in stable arrangements of the oppositely charged ions by means of electrostatic forces (**Coulomb forces**). In this case, we say that there is an **ionic** or **heteropolar** (chemical) **bond** between the two opposite charged ions, one cation and one anion.



The above "story" does not end between a particular cation and a particular anion, as the drawing above shows. The two ions that "have formed the ionic bond" are not isolated from the rest of ions, that is there is no formation of a molecule, as in the case of covalent bond. Each ion is available to form further ionic bonds with other oppositely charged neighboring ions. In this way, ions are held together with Coulomb forces in specific positions in the NaCl crystal. In the crystal, Coulomb forces are exerted in all directions. Each cation is surrounded in the crystal by six anions, and each anion is surrounded by six cations. This "accumulated' structure gives the system minimal energy. That is maximal stability (see Figures 2 and 3). Therefore, in ionic compounds the notion of molecule does not exist. The chemical formula, e.g. NaCl, shows the simplest integral proportion of cations and anions in the crystal. In this way, a threedimensional crystal is formed.

The word 'ion' is derived from Greek, and means 'moving'. This is because during the phenomenon of electrolysis, ions move toward the oppositely charged electrode.

Coulomb force

Between a cation and an anion an *electrostatic* force (**Coulomb force**) is exerted. This force is larger, the larger the charges of the two ions are, and the smaller the distance between the two nuclei.

Because the concept of molecule does not apply in the case of ionic compounds, sometimes the term **formal mass** (formerly formal weight) is used instead of relative molar mass (RMS).



Fig. 2. Figural representation of the formation of solid sodium chloride (the common table salt) through the chemical reaction of solid sodium metal and chlorine gas.



Fig. 3. Formation of the NaCl crystal from Na(*s*) and $Cl_2(g)$. Observe the Na⁺, ions that arise after removal of electrons, and have smaller size than Na atoms (the silver-colored spheres). On the other hand, Cl⁻ ions arise after taking in of electrons and have larger size than Cl atoms (green-yellowish spheres). Take also into account that the formation of ionic bonds leads the system to lower energy as the figure demonstrates.



A model of the NaCl crystal structure (extended form).



A perpendicular section of the crystal (first layer of ions).



A perpendicular section of the crystal (second of ions).



The dissolution of NaCl(*s*) in water causes dissociation of ions in the crystal, and as a result the ions move freely in he aqueous solution. This makes the solution to be a conductor of electricity (an electrolyte).



Fig. 4 Representation of the NaCl crystal (compact form) The picture on the right is a photograph of NaCl crystal, as it appears in the macro-world.

B 1.3 Crystals

A **crystal** is a solid material in which the structural units (atoms or molecules) are placed in an ordered, repeated arrangement in space. In this way, a *three-dimensional periodic structure* is formed. The macroscopic symmetry of the crystal is due to this structure.

When the periodicity of the structure is repeated the same in the whole volume of the crystal, then the material makes a **single crystal**. Most *precious stones* are single crystals. Most crystalline materials are *multi-crystalline*, that is, they consist of a very large number of tiny single crystals. On the other hand, there exist solid materials that do not exhibit any periodicity in their structure, for instance glass; these are called **amorphous** materials.

A special category of crystals are *liquid crystals*. These are a state of matter that many organic crystal substances acquire on melting or on dissolution in certain solvents. A characteristic feature of liquid crystals is that by applying to them an electric or a magnetic field, their molecules orient themselves on the direction of the filed. This property finds applications in TV, PC and telephone screens, in digital watches etc. (see picture).

The crystal structure is characterised by what is termed the *space lattice* and the *elementary cell* or *unit cell* (Fig. 5). There are 7 crystal systems. The one with the largest symmetry has the cube as unit cell and is called *cubic system*. In order of reduced symmetry, the seven crystal systems are as follows:

Cubic, hexagonal, square, trigonal, orthorhombic, monoclinic, and triclinic.



Liquid crystals

The melting of molecular crystals of large molecules (macromolecules) of polar organic compounds has as result that their long, barshaped molecules maintain in many cases, part of the crystal order in liquid state.

The seven crystal systems

Figure 5 shows an example of a **space lattice**. In this, around each point, the other points are distributed in the same manner. On the points of such a lattice, the atoms or molecules of the crystalline substance are placed. The figure also shows the **elementary cell** or **unit cell**. The macroscopic crystal is made by the periodic repetition in space of the unit cell.



Fig. 5 Space lattice with unit cell.

In the unit cell, we define a system of *crystallographic axes*, as Figure 6 shows.



It can be demonstrated that there are seven such different systems of axes or *crystallographic systems*. The *cubic system* has the largest symmetry, and is characterised by the relations: $\vec{a} = \vec{b} = \vec{c}$ and $\hat{\alpha} = \hat{\beta} = \hat{\gamma} = 90^{\circ}$. The *triclinic* system has the smallest symmetry, with: $\vec{a} \neq \vec{b} \neq \vec{c}$ and $\hat{\alpha} \neq \hat{\beta} \neq \hat{\gamma}$.

How the crystal structure is determined

The structure of crystals is determined by means of the method of X rays. X-rays demonstrate the basic features and behaviour of light, that is, they are *electromagnetic radiation*. One feature is *diffraction*, that is deviation of the radiation from linear transmission when it must pass through a small hole or grating (when it encounters a small-sized obstacle). (Figure 7).



Fig. 7 Diffraction of visible light.

Crystals have the property of diffracted X-rays. In this way, the branch of crystallography has evolved, which by means of X-ray diffraction reveals the structure of crystals, that is it reveals the positions and distances of the atoms or molecules in the crystal lattice.

Electromagnetic radiation

It is a kind of energy that is transmitted, even in vacuum, in the form of electromagnetic waves, that is, changes in space and time of the electric and the magnetic field.



X-rays are emitted by different metals that are bombarded with electrons inside the cathode-rays tube.

X-rays and their diffraction by crystals

X-rays are *electromagnetic radiation*, with energy larger than the energy of visible-light radiation. The German physicist Roentgen discovered them in 1895. They owe their name to the then unknown nature. Devices that are called X-rays lamps or X-rays tubes produce them.

The wavelengths of X-rays are small (around 1 Å). For this reason, they can penetrate at sufficient depth through opaque materials. To this property, as well as their different absorption by different materials, their application in medicine is based (X-ray diagnostics).

Diffraction

Diffraction is the phenomenon that is caused during the transmission of a wave through a small hole or grating or when it encounters an obstacle (a barrier). It is connected with the deviation of light from its linear transmission. The phenomenon becomes more evident as the dimensions of the gratings approach the wavelength of the radiation,

A crystal constitutes a natural three-dimensional barrier (obstacle) causing diffraction of X-rays. The reason is that the distances between the atoms or the molecules of the crystal (which constitute the diffraction centres for X-rays) are of the same order of magnitude as X-rays (~ 1 Å).

Crystallography is the study of X-ray diffraction by crystals. If we know crystal structure, we can calculate the wavelength of radiation. Conversely, if we know the wavelength of the radiation, we can uncover the crystal structure. Crystallography studies the pattern in which atoms or molecules are arranged in a crystalline solid. It has applications in chemistry, physics, geochemistry, mineralogy, metallurgy, and even in biology. Through crystallography, the double-helix structure of the DNA (*deoxyribonucleic acid*) was discovered in 1953. DNA is the basic molecule of life.



Ex-ray photo of hand