Chemistry for Civil Engineers-
Supplementary Academic Educational Material

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Author’s acknowledgement
Adam S. Kapcsos
Preamble

Shall not one day of thy life go in vain,
Shall the age of knowledge and reason reign
The table is set; game is on; set sails!
Behold how much science daily unveils.

The World is a lot more than meets the eye
and fortune favours the brave and unshy
thus fear no unknown, lack never the skills
to never give up and conquer all hills.

Wisdom of forefathers lingers still here,
Endeavours, achievements alumni; peer,
Their life was worthy but how about thine?
Enough life possessed to have wasted time?

Chisel, learn, acquire new every day,
Discover, explore, care not what they say.
Carry on and the World will know thy name
as a mind brighter than Hydrogen flame!

(Adam S. Kapcsos: The Journey, 2015)
Week 1: The structure of materials, the built-up of molecules
1. The structure of materials. The concept and structure of matter

Chemistry, as such, is a natural science dealing with materials. It specifies property changing material transformations.

The concept of material has changed a lot over time. Since the beginning of the XXth Century not only do we have to consider corpuscular particles (having steady state mass) as matter, but the beam of light, the electromagnetic vibration and the gravitational potential fields as well.

![Classification of matter by its chemical constitution](image1)

1.1. The atomic structure. Elementary particles

a) Parts of the nucleus

Out of the elementary particles, on the basis of the experiences acquired by nuclear chemistry, the proton (symbol: \( p \)) and the neutron (symbol: \( n \)) are regarded as stable constituents of the nucleus. The (steady state) atomic mass of a proton: \( m_p = 1.672614 \times 10^{-27} \text{ kg} \) (1,007277 relative atomic mass unit [amu]), and that of a neutron: \( m_n = 1.674920 \times 10^{-27} \text{ kg} \) (1,008665 relative atomic mass unit [amu]). The proton and the neutron together are called nucleon. The number of the protons situated within the nucleus is denoted with \( Z \), while in case of neutrons \( N \) is used for the same purpose. A mass number, \( A = N + Z \) (Figure 2.)

![Atomic number, symbol, mass number](image2)
At the beginning of the Periodic table of elements, stability of the nucleus is maintained by the protons and neutrons approximately equal in number, although more neutrons are necessary to stabilise nuclei of higher atomic number. (Figure 3.) The number of neutrons belonging to given number of protons may vary between certain internals. Since chemical properties are determined by the nuclear charge, atoms of the same nuclear charge (atomic number) but of different atomic weight are practically having the same chemical properties. These atom-like structures are located on the same spot in the Periodic table therefore, they are called isotopes.\[1\] The Carbon for instance has 6 isotopes. With Z=6, N= 4-9 is possible. The most frequent one is the mass number 12, C isotope (98,81%) also being the reference point of the relative mass scale.

Isotope:

\begin{quote}
any of two or more forms of a chemical element, having the same number of protons in the nucleus, or the same atomic number, but having different numbers of neutrons in the nucleus, or different atomic weights. There are 275 isotopes of the 81 stable elements in addition to over 800 radioactive isotopes, and every element has known isotopic forms. Isotopes of a single element possess almost identical properties. (http://dictionary.reference.com/browse/isotope)
\end{quote}

There are atoms of various atomic numbers but identical mass numbers. They are known as isobars. Nowadays we are aware of the highly complex built-up of an atom. A number of sub-atomic elementary particles have been successfully identified and characterised through artificial nucleus transformations and cosmic observations such as the positron, the antiproton, the antineutron, the neutrino, mesons, hyperons etc.

Isobars:

\begin{quote}
are atoms (nuclides) of different chemical elements that have the same number of nucleons. Correspondingly, isobars differ in atomic number (or number of protons) but have the same mass number. An example of a series of isobars would be \(^{40}\)S, \(^{35}\)Cl, \(^{40}\)Ar, \(^{40}\)K, and \(^{40}\)Ca. The nuclei of these nuclides all contain 40 nucleons; however, they contain varying numbers of protons and neutrons. The
\end{quote}
term “isobars” (originally “isosbares”) for nuclides was suggested by Alfred Walter Stewart in 1918. It is derived from the Greek word isos, meaning “equal” and baros, meaning “weight”.

(https://en.wikipedia.org/wiki/Isobar_(nuclide))

b) Structure of the electron shell

The nucleus and the protons within are surrounded by the same number of electrons (e). The atom itself is neutral outwards to the exterior.

The formation of detailed theories in connection with the atom and the structure of its electron shells moreover the experimental results of spectroscopy had great influence on some of the basic laws an theories of nowadays’ physics such as Plank’s Quantum Theory (1900), and The Equivalence and Photon Theories of Einstein (1905). The later has become one of the most important electron shell structure investigation methods.

According to Planck’s Quantum Theory the energy, when heating an object radiates out in $h\nu$ size portions, in energy quanta. The Planck’s constant $h$ (universal constant), quantified as: $h=6.626176\times 10^{-34}$ Js, being the frequency $\nu$ of the radiation.

Under the term of Einstein’ Equivalence Theory there is a correlation between a corpuscular system and a frequency $\nu$ radiation (e.g.: light) in interaction having exchanges in mass and energy. That correlation between the change in energy ($\Delta E$) and the frequency being:

$$\Delta E=h\nu$$

Einstein called this electromagnetic $h\nu$ radiation unit a photon.

Example for interaction:

$AgBr$ (photography commodity) + photon ($h\nu$)

$Br^- + photon \rightarrow Br + e$, furthermore $Br + Br \rightarrow Br_2$

$Ag^+ + e \rightarrow Ag$ (this can be seen on the photo disc)

Bohr created two postulates about the structure of the electron shell relying on the Quantum and Photon Theories:

- The Quantum Theory of Stationary Orbits: electrons can only orbit around the nucleus on discrete trajectories (paths, orbitals) with certain energy without emitting radiation of any kind. While skipping from one orbital to another, the electron changes its energy. The change in energy is skip-like.

- According to the Frequency Theory the following correlation holds for electromagnetic radiation emitted or absorbed by the atom and the energy change of the electron:

$$E = E_1 - E_2 = h\nu$$
Where $E_1$ and $E_2$ are possible energies at two orbitals. The energy difference between the two stages in case of a migration of a single electron is one photon. That is why the spectrum of atoms is linearly structured.

Bohr’s atom model describes the Hydrogen atom with high precision although it is not applicable to the atoms of other elements. To characterise the state and number of electrons within an electron shell moreover to explain the changes of spectral line at spectroscopy experiments, *four quantum numbers* were introduced (whose physical interpretations were formed by Sommerfeld).

Principal quantum number: $n$

\[ n = 1, 2, 3 \]

K L M (electron shell)

(The energy level K belonging to the principal quantum number $n = 1$ means the lowest possible energy level and a location closest to the nucleus.)

Azimuthal quantum number (also known as angular quantum number or orbital quantum number): $l$

\[ l = 0, 1, 2, ..., n-1 \]

s p d….(electron state, spatial shape, orbital, **Figure 4.**)

Magnetic quantum number

\[ m = -l, -l+1, ..., 0, ..., l-1, +l \]

(Magnetic angular momentum generated by orbital movement)

Spin projection quantum number: $s$

\[ s = + \frac{1}{2}, -\frac{1}{2} \]

(Describes the spin, the intrinsic angular momentum)
Rules governing the built-up of the electron shell:

**Pauli Exclusion Principle:** No two electrons in an atom can have identical quantum numbers.(all 4 of them)

**Hund’s rule:** On a given electron shell with a given number of electrons, the electrons are located so that as many of them is unmatched as possible. In other words, every orbital in a sub shell is singly occupied with one electron before any other orbital is doubly occupied.

The electron structure of the elements is shown in periods 1, 2, and 3 of the periodic table of elements. In Figure 6, the electron structure of some elements is depicted with the conventional denotations.
1.2. The structure of the molecules. Types of chemical bonds

The molecules, as those smallest particles of compounds that exist independently having the chemical properties of the compound at hand, are built up of atoms. The atoms are held together by bonds within the molecule. Upon binding the original electron shell layout of the atoms is rearranged consequently molecules are not mere sets of atoms but new formations as far as the properties go.

There are two main types of chemical bonds and therefore there are two basic types of chemical compounds. In case of the first bond type, the atoms forming the molecule have electric charge while in case of the second bond type atoms have no.

The first type of bond is called ionic or heteropolar while the other main type is referred to as covalent or homopolar bond.

Between these two extreme cases can be found those compounds whose bond type is intermediate i.e. polar bond and the compounds comprised of atoms interconnected via intermediate bonds are called polar compounds.

In each and every case, the outermost electron shell structure is rearranged however; the rearrangement can only assume such proportions that the Pauli Exclusion Principle is complied with regarding the molecule as a whole. For instance, even the mutual newly formed electron shell made of the respective electron shells of the atoms forming the molecule cannot contain two or more electrons identical in all four quantum numbers.

The manner in which the bond is created significantly depends on how heavily attracted are the electrons within the atom playing a role in the formation of the bond as well as the electron negativity of the adjacent atoms. The electrons situated in the electron shell of solitary neutral atoms can be removed by the application of the so-called ionisation energy. (Electrons are the easiest to detach from alkali metal atoms) It also comes with change in energy when an electron is integrated into the electron shell of a neutral atom. This energy change is called the electron affinity. (The experimental determination of the electron affinity is somewhat more difficult than that of the ionisation energy.)

**electron affinity:**

is a measure of the energy change when an electron is added to a neutral atom to form a negative ion. For example, when a neutral chlorine atom in the gaseous form picks up an electron to form a Cl⁻ ion, it releases an energy of 349 kJ/mol or 3.6 eV/atom. It is said to have an electron affinity of -349 kJ/mol and this large number indicates that it forms a stable negative ion. Small numbers indicate that a less stable negative ion is formed. Groups VIA and VIIA in the periodic table have the largest electron affinities. ([http://hyperphysics.phy-astr.gsu.edu/hbase/chemical/eleaff.html](http://hyperphysics.phy-astr.gsu.edu/hbase/chemical/eleaff.html))

The electron transfer from one atom to another only takes place deliberately if the transfer comes with release of energy. The electron withdrawing ability of the atom is called electron negativity and is quantified on the Pauling scale (Table 1.), whose arbitrarily chosen reference point is the 2. 1 value associated with the Hydrogen. The electron negativity is a one-dimensional numerical data that indicates the measure by which an atom is able to attract its bond-forming electrons in comparison to other atoms.
The electron transfer is in correlation with the mutual measure of ionisation energy (I) and electron affinity (E). If the difference in electron negativity between two bond-forming atoms is great, then ionic bond, if subtle or none then covalent bond, and if medium then polar bond is created. Consequently, it depends on the joining atom as well if ionic or covalent bond is created. Larger the bond-forming energy release, the more efficient the bond-forming electron transfer. At compound creation, usually the motive force is to reach stability i.e. to form a creation of smaller energy content. The energy content of a molecule is smaller than the sum of the energy of the constituting free atoms. The energy difference is equal to the binding energy.

### Week 1 Video session:

https://www.youtube.com/watch?v=sj6YHzs6q6w

https://www.youtube.com/watch?v=accyCUzasa0

https://www.youtube.com/watch?v=OLCqaWaV6jA

### Week 1 Question session:

**What is the difference between the atomic number and the mass number of an element?**

List and describe the rules governing the built up of the electron shell, the types of quantum numbers and Bohr’s postulates.

**Give the definition of isotopes, isobars, electron affinity, electron negativity and ionisation energy.**
Week 2: Types of chemical bonds and their characteristics
The chemical bonds are classified on the basis of the strength of the bond usually into two categories:

*Primary bond* (80–800 kJ/mol): ionic, covalent, dative and metallic bond

*Secondary bond*:
- Hydrogen bond (hydrogen bridge), 20–40 kJ/mol
- Van der Waals bonds, 0.4–8 kJ/mol

**Ionic bond, ionic compounds**

An ionic bond is formed, when two or more atoms of largely different electron negativity approach one another and the valence electrons of the smaller electron affinity atoms are transferred to the atom with the highest electron negativity. By this, the former becomes a positive and the latter a negative ion. The compound now received is held together by the electrostatic forces exerted by ions of opposite charges on one another. At ionic bonds the bond-forming electrons belong only to the atom taking them up. **Figure 7.** illustrating the changes taking place at Sodium-Chloride molecule formation.

![Figure 7](image)

**Figure 7.** The formation of ionic bond through the example of NaCl [6]

\[
\begin{align*}
\text{Na:} & \quad (1s)^2(2s)^2(2p)^6(3s)^1 \\
\text{Cl:} & \quad (1s)^2(2s)^2(2p)^6(3s)^5
\end{align*}
\]

The formation of ionic compounds induces change in size, the *cation* shrinks the *anion* expands with respect to the size of the original atom. **Figure 8.**

![Figure 8](image)

**Figure 8.** Change in size in case of ionic bond formation [7]
As a result of the electron transfer, the \(s^2p^6\) electron octet, noble gas configuration is formed on either ion. From the central elements of the periodic table no ionic compound is formed.

### Covalent bond

The molecule is created with the mediation of the so-called *valence electrons* situated in the outermost, incomplete shell of atoms. The electrons of the bonding electron pair spend adequate amount of time in the vicinity of either atom. The *electron shells* overlap. The mutual electron pair has to have opposite spins. *Homonuclear* covalent bond is created between identical atoms. **Figure 9.** depicting the bond formed in case of Hydrogen and Fluoride molecules.

![Homonuclear diatomic compounds: H\(_2\), Cl\(_2\), O\(_2\), N\(_2\) ... share electrons equally = NON POLAR COVALENT BOND](image)

**Figure 9.:** The formation of homonuclear covalent bonds [8]

The examples showcased indicate that both the noble gas configuration is realised both in case of the Hydrogen and the Fluoride molecule. The molecules are not polar. *Heteronuclear* covalent bond is formed at different atoms joining up. **Figure 10.** showing the covalent bond of water, hydrochloric acid, and ammonium, moreover the molecular orbital created around a Hydrogen-fluoride molecule.

![Heteronuclear covalent bonds (H\(_2\)O, HCl, NH\(_3\), HF)](image)

**Figure 10.:** Heteronuclear covalent bonds (H\(_2\)O, HCl, NH\(_3\), HF) [9]
In this case the bonding electrons spend more time (can be found more frequently) around the atom that exerts greater attractive force. The molecule is reshaped into a dipole molecule where the centroids of the charges do not coincide. The distinctive dipole moment of a dipole molecule: \( \mu = e \cdot l \), where \( l \) is the distance between the two charge centroids, \( e \) is the magnitude of the charge. The magnitude of the dipole moment is influenced by the electron negativity difference of the bonding atoms, moreover if the external electrons are not identical (s-p).

This means that for instance, in a HF molecule, certain ionic properties of H and F respectively are preserved to some extent consequently the leftover electrostatic attraction is taking part in the stabilisation of the bond as well.

In case of multi atom molecules, even within one molecule, s-s, p-s and p-p bonds can occur alike. Especially when the number of the parallel-spin unmatched electrons, can be increased with relatively small amount of energy invested, over the figure of the one under the term of Hund’s rule. The energy equalisation is completed (hybridisation). The bond created via such electrons is a hybrid bond.

**Hybridisation:**

In chemistry, hybridisation (or hybridization) is the concept of mixing atomic orbitals into new hybrid orbitals (with different energies, shapes, etc., than the component atomic orbitals) suitable for the pairing of electrons to form chemical bonds in valence bond theory. Hybrid orbitals are very useful in the explanation of molecular geometry and atomic bonding properties. Although sometimes taught together with the valence shell electron-pair repulsion (VSEPR) theory, valence bond and hybridisation are in fact not related to the VSEPR model ([https://en.wikipedia.org/wiki/Orbital_hybridisation](https://en.wikipedia.org/wiki/Orbital_hybridisation)).

The excitation energy is made up for by the binding energy. Such change takes place, for instance in the outermost electron shell of Oxygen at water molecule formation.:

\[
\text{O}_2: (1s)^2 (2s)^2 (2p)^4 \\
\text{O}_2: (1s)^2 (2s)^2 (2p_x)^2 (2p_y)^1 \rightarrow (1s)^2 (2h_1)^2 (2h_2)^2 (2h_3)^1 (2h_4)^1
\]

**Excitation:**

In physics, the addition of a discrete amount of energy (called excitation energy) to a system—such as an atomic nucleus, an atom, or a molecule—that results in its alteration, ordinarily from the condition of lowest energy (ground state) to one of higher energy (excited state). ([http://www.britannica.com/science/excitation-energy](http://www.britannica.com/science/excitation-energy))

Two electron pairs, of already compensated spins, s and p also influence the bonding as the tetrahedral molecular structure is distorted. **Figure 11.**

**Figure 11:** Tetrahedral structure in case of the Methane (having no free electron pair), the Ammonium (having one free pair of electrons) and the water (two free pairs of electrons).[4]
**Dative bond**

There are such compounds in which the atoms are of such kind that no noble gas configuration can take shape around them neither through electron transfer nor via electron pair formation. Such type is, for instance, the fairly stable Carbon-dioxide (CO). Originally C has two pairs of unmatched valence electrons and so does the Oxygen.

\[ \text{C: } (1s)^2 (2s)^2 (2p)^2 \]
\[ \text{O: } (1s)^2 (2s)^2 (2p)^4 \]

With the bonding of the two-two unmatched electrons however, no electron octet can be formed around the Carbon:

![Diagram of C and O bonding](image)

The \(s^2p^6\) configuration can only be realised if one more pair of electrons of the Oxygen is taking part in the bonding according to the followings:

The Oxygen providing the extra pair of electrons is the *donor*, the Carbon taking up the electron pair is the *acceptor*.

There is no conceptual difference between the covalent and the dative bond the latter however implies charge asymmetry. The molecule becomes dipole. The Oxygen would have a partially negative, the Carbon, a partially positive charge. Dative type of bond can only take shape if the donor has any free electron pair and the acceptor is short of two electrons in its valence shell. The so-called *onium ions* are also created with dative bonds (complex ions, polyatomic ions) connection a molecule and an ion. Such ion is the Ammonium ion (NH\(_4^+\)):

and the Oxonium ion (Hydronium) (H\(_3O^+\)):

In the positively charged Ammonium ion, out of the electrons of the 4 H atoms only three are necessary to build up a mutual electron shell of noble gas configuration, while in case of the Oxonium out of the 3 H atom electrons only 2 are needed.

**Metallic bond**

In a metallic bond, the positively charged metal ions are surrounded a cloud, a shell of delocalised electrons. The electrons released by the metallic atoms belong to all the metallic ions alike. Metallic bond can only occur in metal crystal structures (there are atoms in vapour state present) therefore, for a more detailed qualification please see metallic grid structures later.
Hydrogen bond

Hydrogen bonds are polar covalent molecules, more precisely a guided ionic bond of electrostatic nature between the latter and the appropriate atoms. It is observable between molecules and atoms if the polar covalent molecule’s, (NH$_2$, H$_2$O, HF, etc.) Hydrogen can establish contact with atoms of large electron negativity (F, O, N) Figure 12.

Figure 12.: Formation of Hydrogen bond in case of a) HF, b) HCOOH (Formic acid/Mechanic acid) and c) H$_2$O [4]

The atomic diameter of H is exceptionally small, having one electron that is capable of exerting effect from point blank range. Its effect creates a bond of paints and other excipients on textile fibres, causes the solubility of certain organic compounds in water, responsible for the unusually high boiling point of molecules containing OH and NH groups, furthermore, without Hydrogen bridge type of bond water would be gaseous even at comparatively low temperature.

Hydrogen bridge:

A hydrogen bond is the electrostatic attraction between polar molecules that occurs when a hydrogen (H) atom bound to a highly electronegative atom such as nitrogen (N), oxygen (O) or fluorine (F) experiences attraction to some other nearby highly electronegative atom. These hydrogen-bond attractions can occur between molecules (intermolecular) or within different parts of a single molecule (intramolecular). The hydrogen bond (5 to 30 kJ/mole) is stronger than a Van der Waals interaction, but weaker than covalent or ionic bonds. This type of bond can occur in inorganic molecules such as water and in organic molecules like DNA and proteins. ([https://en.wikipedia.org/wiki/Hydrogen_bond](https://en.wikipedia.org/wiki/Hydrogen_bond))
Van der Waals bonding forces

In the majority of the cases bonds between molecules are not established via Hydrogen bridge but the created by the so called Van der Waals forces. They take their origin from the fact that even the covalent molecules are not all uncharged but some of them possess dipole moment due to their polarisation. These results in an electrostatic interaction and those are the Van der Waals forces. Usually three types of effects are distinguished:

Orientation effect: orientation of molecules with dipole moments of the same magnitude.

\[
\begin{pmatrix}
+ \\
- \\
\end{pmatrix} 
\rightarrow 
\begin{pmatrix}
+ & + \\
- & - \\
\end{pmatrix}
\]

Inductive effect: Charge symmetry is induced by the dipole in a molecule originally lacking dipole moment.

\[
\begin{pmatrix}
- \\
+ \\
\end{pmatrix} 
\rightarrow 
\begin{pmatrix}
- & + \\
+ & - \\
\end{pmatrix}
\]

Dispersion effect: An interaction caused by the so called dispersion forces between molecules originally with charge symmetry.

\[
\begin{pmatrix}
+ \\
+ \\
\end{pmatrix} 
\rightarrow 
\begin{pmatrix}
- & + \\
+ & - \\
\end{pmatrix}
\]

The strongest is the orientation effect while the weakest being the dispersion effect. Such forces are present, for instance, between the molecules of gases and liquids, the latter are solitary systems having own volumes mainly because of the Van der Waals forces.

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Week 2 Video session:

https://www.youtube.com/watch?v=lkl5cbfqFRM

https://www.youtube.com/watch?v=uIVh_xNvcJ4

https://www.youtube.com/watch?v=GRDmlldPtc0

Week 2 Question session:

Classify the chemical bonds strength-wise and define the ionic, metallic, dative and hydrogen bonds.

Qualify the difference between the covalent and the dative chemical bond.

Essay: Van der Waals bonding forces.
Week 3: Phase-based classification and characterisation of material systems. Gas and liquid systems

ideal gas, real gas, Boyle-Mariotte law, Gay-Lussac laws, Universal Gas law, critical temperature, mean free path, cohesion force, Avogadro’s law, Newtonian liquid, diffusion, viscosity, flow profile, thixotropy, dilatancy, compression
2. Classification and characterisation of matter systems (Classification based on phases)

2.1. Gas systems

Gas laws

With the exception of monatomic noble gases and vaporised metals, gases are systems comprised of molecules. Within these, the Van der Waals forces are so subtle that they are unable to bond the molecules to one another therefore; gases have no respective shape or volume moreover they always fit into a container of any size distributed evenly.

We speak about an *ideal gas* if the intermolecular attracting forces are completely omitted and a point like, elastically bouncing molecule is supposed with negligible extent in comparison to the size of the gas space. This is an ideal boundary state in which at moderate pressure and adequate temperature fairly good approximations are possible. The *Boyle-Mariotte law* is valid for the ideal gas:

$$(pv)T = \text{constant}$$

(at constant temperature the product of the pressure and volume of the gases is constant) The law is also a hyperbolic function. Figure 13.

The change in pressure and volume of the gases by temperature is described by Gay-Lussac’s laws.

*Gay-Lussac’s 1st law*: The volume of the gas at $t \degree C$, $p=\text{constant (isobar)}$ and under these circumstances is:

$$v_t = v_o + v_o/273.15 \cdot t = v_o (1 + \alpha t)$$
where \( v_0 \) – the volume of the gas at 0 °C
\( \alpha \) – heat expansion coefficient (1/273.15)

Gay-Lussac’s 2\textsuperscript{nd} law: The pressure of the gas at t °C, \( v=\)constant (isochore) and under these circumstances is:

\[
p_t = p_0 + \frac{p_0 \cdot 273.15}{1°C} \cdot t = p_0 (1 + \alpha t)
\]

where 
\( p_0 \) – the pressure of the gas at 0 °C
\( \alpha \) – tension coefficient (1/273.15)

To the ideal gases the Universal Gas law is valid :(Boyle-Mariotte-Gay-Lussac):

\[
p \cdot v = p_0 \cdot v_0 (1 + \alpha \cdot t)
\]

Taking into consideration that:
- Under the term of the Avogadro’s law in equal volumes of ideal gas spaces at the same temperature and pressure the same number of molecules can be found.
- The temperature is not calculated with respect to the melting point of the ice but the 0:

\[
t = -273.15 °C
\]
\[
T = t + 273.15 °C, \ t = T - 273.15 °C
\]

The melting point of the ice in Kelvin
\( T_0 = 273.15 \) K to 1 mole of gas (the unit is mol) at 1 bar is:

\[
\frac{P_0 \cdot V_0}{T_0} = R
\]

\[
p \cdot v = p_0 \cdot v_0 (1 + \frac{T - 273.15}{273.15})
\]

R – universal gas constant
The Universal Gas law to:

1 mole of gas: \( P \cdot V = R \cdot T \)

to n mole of gas: \( P \cdot V = n \cdot R \cdot T \)

The majority of the naturally occurring gases, especially at a high pressure is a real gas.
In case of real gases the product of \( pv \) is not constant but is dependent on the pressure, \((pv)T = f(p)\). The p-v isotherm of the real gases is different from that of the ideal ones. (Figure 13.: Real gases and Figure 14.)
The Universal Gas law describing the \( p, v, T \) correlation of gases had to be modified as the introduction of such member \((a/V^2)\) was necessary that takes into account the mutual attraction of the molecules and the cohesion that increases the pressure, moreover another
factor that (b) that takes into consideration the respective volumes of the molecules. This consideration shrinks the space available to molecular movements therefore it is to be subtracted from the $V$ total volume.

According to the aforementioned, the equation of state of Van der Waals concerning real gases is:

$$
\text{to 1 mole of gas: } \left( p + \frac{a}{V_m^2} \right) * (V_m - b) = R \cdot T
$$

$$
\text{to } n \text{ mole of gas: } \left( p + \frac{n^2a}{V^2} \right) * (V - n \cdot b) = n \cdot R \cdot T
$$

a: cohesion constant
b: volume constant
These two vary from gas to gas

Figure 14.: The Van der Waals isotherms of CO$_2$ [4]
The higher the temperature the more resemblance the curves of the gases show with that of the ideal gases. The equation with respect to V is third order, at the critical temperature \((\text{CO}_2 : T_{Kr} = 304 \text{ K})\) and temperatures below it, 3 volumes belong to one pressure state which is impossible in case of a one phase (gaseous) system. Liquid has to be present; at point „E” liquefaction is finished, the \(\text{E\text{E}}\) branch corresponds to the pure liquid. Above the critical temperature liquefaction is not possible. Water above 370 °C does not condensate \((\text{H}_2\text{O}: T_{Kr} = 370 \text{ °C})\).

**Movement of gases**

Gas molecules are in constant motion: They carry out rotation and translational movements simultaneously, furthermore, the atoms within do oscillatory motion. The velocity of molecules at normal pressure is approx. 100 m/sec, however turning on the gas tap the smell of gas is only observed somewhat later. This phenomenon can be explained with the constant collisions as molecules follow zigzagged orbitals therefore their average displacement is small.

![Diagram](image)

To characterise the movement of gases the concept of the *mean free path* \((\lambda)\) was introduced:

\[
\lambda = \frac{A}{\rho_{\text{gas}}} \quad (\lambda)V,T = \frac{A'}{p_{\text{gas}}}
\]

The mean free path is inversely proportional to the density of the gas \((\rho_{g})\), and the pressure of the gas \((p_{\text{gas}})\) at a given temperature and volume. \(A\) and \(A'\) are material constants.

The mean free path is one of the factors of the *diffusion* of gases. (Sprinkling drops of Bromine to the bottom of a glass vessel, though the molecules being heavier than particles of air, drops make it to the top of the vessel. If the pressure is decreased or the temperature is increased, the process is speeded up. The collision and bouncing of the molecules against the wall of the vessel causes the *pressure* of the gases.)

*Diffusion:*

*Also called migration. An intermingling of molecules, ions, etc., resulting from random thermal agitation, as in the dispersion of a vapor in air. It can mean as well a reflection or refraction of light or other electromagnetic radiation from an irregular surface or an erratic dispersion through a surface; scattering.*

(http://dictionary.reference.com/browse/diffusion)

**2.2. Liquid systems**

The real gases at temperatures below their critical ones and with the right pressure can be compressed to liquids. The liquid state can also be approached from the direction of the solid phase as by heating a solid matter it changes phase to liquid, at its melting point becoming a melt.
Just like in case of the gases, liquids have no own shapes and always fit in a container of some size rather tightly. Although, between liquid molecules the bond strength is comparatively great as the so-called cohesion forces are there. These forces keep the molecules in condensed form but maintain the possibility of thermal movements (hence the lack of own shape). Apart from the attraction there is repulsion between the molecules as well. The repulsive forces act observably mainly when molecules are approached to one another beyond a certain extent. Therefore the compressibility of the liquids is rather small. Motion-wise, molecules mainly carry out rotation and oscillatory motion. One of the distinctive features of the liquids is the viscosity or internal friction. Inside the liquid the prevailing attracting forces between the molecules compensate each other in steady state. Two layers of liquid next to one another, moving in opposite directions (shearing) are capable of exerting some sort of resistance against the displacement. Figure 15.

![Figure 15: Layers being displaced within the liquids](image)

The magnitude of the appearing friction force (F):

\[ F = \eta \cdot A \cdot \frac{v}{d} \]

where \( \eta \) = internal friction or viscosity.

The unit of the viscosity: \( \text{Nm}^{-2}\text{s} = \text{Pas} \),
in practice: mPas (milli Pascal sec)

The viscosity obtained like that is called dynamic viscosity. The viscosity is very important from the viewpoint of the practice, for instance, at dimensioning streams of liquid in pipelines, operating pumps, slopes, sedimentation and settling of silts etc.

![Figure 16: Flowing liquid interaction with solid surface](image)

At a stream interacting with a solid surface laminar flow is created: the liquid layers are displaced in the same direction but with different velocities with respect to the surface. The smallest displacement is performed by the layer stuck to the solid surface. In a tube of small
diameter a flow profile is formed. The behaviour of the ideally viscous (*Newtonian liquid*) is described by the a Newton law:

\[ \tau = \eta \cdot \frac{dv}{dy} = \eta \cdot \gamma \]

where
- \( \tau \) the shear stress (shear force/area), its unit being Pa
- \( v \) the linear velocity of the consecutive layers (dx/dt), \( dv/dy = \gamma \) the velocity gradient (slope of velocity), unit: s\(^{-1}\)

In case of permanent flow, dynamic equilibrium is ensued.

**Rotation curve types (Figure 17)**

In case of a *Newtonian liquid*, by increasing \( \tau \), and \( \gamma \) viscosity is unchanged (\( \eta = \) constant, [Figure 16. curve 1.](#))

The liquids showing *structural viscosity* tend to be less viscous with increased shear stress and with decreased velocity gradient. That is how liquid systems containing aggregated particles behave as the adhesion is dissipated between the particles due to shearing or in case of rod systems built up of rod like particles, the particles are arranged into the direction of the flow as a result of which viscosity is decreased again. ([Figure 16. curve 2.](#))

The phenomenon in which \( \eta \) is increasing by shear stress and velocity gradient is called dilatancy.

*Dilatancy*:  
*a phenomenon caused by the nature of the stacking or fitting together of particles or granules in a heterogeneous system, such as the solidification of certain gels under pressure, and the thixotropy of certain gels.* ([http://www.thefreedictionary.com/dilatancy](http://www.thefreedictionary.com/dilatancy))

It is appearing for instance, when as a result of sudden pressure the particles are unable to evade each other and are congested. ([Figure 17. curve 3.](#))

The \( \gamma-\tau \) curve of real plastic solids does not depart from the origin but from a defined \( \tau_B \) value. This is the critical shear stress at which laminar flow is launched, the *Bingham yield stress* limit.

At the get-go of the flow, the intermolecular forces have to be overcome. In a general case structural viscosity is appearing at the liquid systems as well. ([Figure 17. b curve 4.](#) and 4 *)
At systems having a yield stress and structural viscosity a phenomenon that is known for a long time is often observed, namely the *thixotropy*. (Its name is originated from the 1930s and it means ‘motion upon touch’) e.g.: The bentonite slur/slop is semisolid at rest but becomes liquid upon stirring or shaking just to be in semisolid state once again when the excitation stops.

**Thixotropy:**

*Thixotropy is a time-dependent shear thinning property. Certain gels or fluids that are thick (viscous) under static conditions will flow (become thin, less viscous) over time when shaken, agitated, or otherwise stressed (time dependent viscosity). They then take a fixed time to return to a more viscous state. In more technical language: some non-Newtonian pseudoplastic fluids show a time-dependent change in viscosity; the longer the fluid undergoes shear stress, the lower its viscosity. A thixotropic fluid is a fluid which takes a finite time to attain equilibrium viscosity when introduced to a step change in shear rate. Some thixotropic fluids return to a gel state almost instantly, such as ketchup, and are called pseudoplastic fluids. Others such as yogurt take much longer and can become nearly solid. Many gels and colloids are thixotropic materials, exhibiting a stable form at rest but becoming fluid when agitated.* (https://en.wikipedia.org/wiki/Thixotropy)

The weak adhesion bond between the particles can easily be destroyed by small amount of mechanical energy. The area of the loop on curve $\gamma$-$\tau$ defines the measure of thixotropy (Figure 17. c, curve 5.)

![Figure 17.: Liquid systems rotational curve types [4]](image)

Further important feature of liquids is the density (In Table 2, can be seen the density and viscosity of some matter to compare) and the surface tension (the latter is being dealt with in a later chapter).

<table>
<thead>
<tr>
<th></th>
<th>Density, $\rho$ [g/ml]</th>
<th>Viscosity, $\eta$ [mPas]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hg</td>
<td>13.5</td>
<td>2</td>
</tr>
<tr>
<td>Honey</td>
<td>1.1</td>
<td>$\sim$ 5000</td>
</tr>
<tr>
<td>Bitumen</td>
<td>1.2</td>
<td>$\sim$ 50000</td>
</tr>
</tbody>
</table>

*Table 2.: Density and viscosity of matters (informative data without the denotation of the temperature)*
Week 3 Video session:

https://www.youtube.com/watch?v=ehvLyvwAEYc

https://www.youtube.com/watch?v=RIUEZ3AhvVE

https://www.youtube.com/watch?v=1AESWxko4nl

Week 3 Question session:

State and explain The Boyle-Mariotte law, Gay-Lussac’s laws and the Universal Gas law, the concept of the ideal and real gases, and that of the Newtonian liquids.

What is mean free path Bingham yield stress, viscosity, diffusion, thixotropy, and dilantancy?

Compare and contrast the behaviour of liquid and gas systems in a confined space.
Week 4: Phase-based classification and characterisation of material systems. Crystalline solid matters
2.3. Solid matters

Solid phase materials have constant volumes and shapes. Their most important group is built up of crystals.

2.3.1. Solid matters with crystalline structure

It is typical of the crystalline solid materials that the constitutive atoms, ions or molecules within are arranged in a form of a periodically repeating, uniform latticework. The crystals are homogeneous but anisotropic. That means that a part of their properties (e.g.: density) moreover their chemical composition is uniform all over the crystal. The remaining part of their properties (refraction, electric and heat conductivity) is however, dependent on the orientation, the direction. The latter one is a vectorial feature. The anisotropic nature of crystals can be traced by examining the growth velocity being different in various directions but the same at parallel directions.

Formation and properties of the crystal lattice

If a defined point is displaced by a certain distance in a certain direction and the displacing process (translation) is repeated, the result is a one-dimensional infinite point line, a linear lattice. If the linear lattice is translated in a parallel manner by a certain offset infinitely many times, the result is a two-dimensional grid, a lattice sheet or planar lattice. Finally, if the planar lattice is translated into a plane other than its own infinitely many times, a spatial lattice is obtained. **Figure 18.**

![Figure 18: The structure of the crystalline latticework](image)

The distance between two adjacent points (spatial items) is the elementary translation or lattice constant \(d\). This can be either the same or different in all three directions of the space. The points of the grid are the nodes of the elementary cells. So the elementary cells are such smallest parts of the lattice with which a crystal can be built up if translated in all three directions of the space. The elementary cells can be characterised by the length of their edges (lattice constant) whose order of magnitude is: 0.1 nm, and by the angle enclosed by the edges. The bonding energy of a molar quantity of crystalline solid body is the lattice energy. That much energy is released upon the unification into a crystal of atoms or ions equivalent in
quantity to 1 mole. On the other hand, the same amount of energy is necessary to invest to dismantle the aforementioned lattice to atoms, ions or molecules situated infinitely far from one another. Because of the uniform structure of the crystalline materials their melting point is sharp as the bonds of the same bonding energy disintegrate at the same time.

The most distinctive feature of the crystals is the symmetry. Geology is dealing in depth with various types of crystals differentiated on the basis of symmetry states. The set of elementary cells is broken down into four basic sub-categories:

- Simple elementary cell (mass centres only at the nodes)
- Spatial-centred (mass centres at nodes and at the centroid of the cell)
- Base-centred (mass centres at nodes and in the middle of the top and bottom face of the cell)
- Face-centred (mass centres at the nodes and in the middle of all the faces)

Types of crystal lattices

On the basis of the quality of the particles situated at the nodes and the forces acting between them, crystal lattices can be classified into four main groups.

Ion lattice

In ionic compounds the ions are attached so that the ones of opposite charges are close to each other, while same charge ions are far away. Since ionic compounds are held together by electrostatic forces, there are no prevailing directions. The lattice structure is mainly defined by the fitting of the anions (those are the bigger ones). The cations are located in the voids between the anions. Both in melts and in crystals not molecules but sets of ions are found in stoichiometric proportions. The uniform crystal lattice in which the positive and negative ions sit next to each other regularly is of lower energy therefore more stable than as if the ions would be paired up to molecules.

In the crystal of the NaCl (rock salt, table salt) each and every Na$^+$ ion is directly surrounded by six Cl$^-$ ions. (and every chloride ion is surrounded by six sodium ion). These put together exert greater attracting force on the Na$^+$ than one chloride would be able to exert in the NaCl molecule. The rock salt lattice behaves as though the face-centred lattices of a Sodium and a chloride were pushed into each other with half edge of offset. Figure 19.
Upon heating the rock salt, molecules are put into the steam space since it requires less energy than as though the ions would leave individually the condensed phase. In a NaCl gas molecule, where one sided forces are dominant the ions are closer to each other than in the rock salt crystal lattice. In the crystalline nodes complex ions can take a seat as well. In the lattice of the CaSO4, Ca^{2+} and SO_{4}^{2-} ions are found. The Sulphate-ions are of tetrahedral shape and within them; the Oxygen atoms are a lot closer to the central Sulphur atom than to the rest of the Sulphur atoms. A special type of the ionic crystals is the silicates (micas, feldspar, quartz, etc.). The structure of the silicates can be traced back to the tetrahedral structure of the SiO_{4}^{4-} anion. In these each Silicon atom is surrounded by four Oxygen atoms in tetrahedral layout. (Figure 20.) The laminar lattice structure materials (Aluminium-Silicate-Hydrates) are known for being able to absorb a lot of water and to be prone to swelling. The water molecules are connected via Hydrogen bridges between the layers to each other. (Figure 21.)

![Framework Silicates](image)

**Figure 20.: The crystal lattice of the Silicates [13]**

![Structure of some clay minerals](image)

**Figure 21.: Structure of some clay minerals (to the left Kaolinite, to the right Montmorillonite) [14][15]**
In the ionic lattice the grid members are rather strongly bonded, therefore practically they are nonconductive, less volatile, have a high melting and freezing point and considerable hardness. Because of the ions building up the crystal lattice, many ionic crystal lattice compounds are highly soluble in water.

Molecular crystal lattice

In the nodes, the grid points (apart from noble gases) are double or multi-atom molecules. The molecules are only bonded by weak intermolecular bonds such as Van der Waals or Hydrogen bridge. Consequently the strength of the molecular lattice compounds is low having also a low melting point and being quite volatile. Since there are no free ions within them they are less soluble in water conducting electricity rather bad. Typical representatives of this group are the organic compounds (paraffins, naphthalenes etc.) The ice also forms a molecular lattice in which Hydrogen bridge is the intermolecular bond. In the dry ice (CO₂) the Carbon-dioxide molecules situated at the nodes are connected via Van der Waals forces. (Figure 22.)

![Figure 22. The molecular lattice of the dry ice [4]](image)

Atomic lattice

In the atomic substances oriented, covalent bonds keep the atoms together. The lattice geometry here is not defined by the tight fitting but much rather the oriented covalent bond forces. Typical example being modifications of the Carbon. surrounded by four other equally far from one another a) the diamond is a material. in contrast, the the diamond as one of the Every Carbon atom is Carbon atoms each situated in tetrahedral layout. (Figure 23. transparent, exceptionally hard Graphite is of layered crystal lattice where the individual Carbon atoms only have three adjacent Carbon atoms moreover the interlayer forces are of weak secondary Van der Waals type. (Figure 23. b) The Graphite is greyish, soft, leaves a mark on the paper and unlike the diamond, conducts electric current.
Metallic lattice

While the large electron negativity, i.e.: non-metallic elements form molecules or atoms, the small electron negativity therefore metallic elements create metallic crystal lattices. The metallic atoms unite to form metallic crystals, the detached valence electrons are quite free to move around the positive ions situated in the grid points as the collectively belong to the whole lattice. The metallic bond is not oriented. Connection is established by the mutually used electrons (multicenter bond) with strong metallic bonds similar to covalent bonds. The distinctive features of the metallic bonds of metals can be interpreted on the basis of the Band theory. The less strongly tied 3spd and 4spd electrons undergo fission as metallic atoms approach and more allowable energy levels are formed. The energy bands overlap. Every atom transfers to the widened, now common energy level (band) its valence electrons. (Figure 24.)

If the number of the atoms is large, as a result of the fission the number of the energy levels will also be large.
The conductive, non- or semi conductive properties of the metals and the solids in general can be comprehended with the help of the Band Theory. (Figure 25.) Between the bands there are the so-called forbidden bands. For instance, the diamond is nonconductive because the complete valence band and the completely empty conductive band are separated by a wide forbidden band. In case of Sodium, the whole valence band is not complete; therefore an electron can be transferred to the conductive band with relatively small amount of energy. At semi-conductors, the forbidden band is small. Because of the free delocalised electrons present in the metallic lattice, such materials are great at conducting heat and electricity. The electric conductivity of metals decreases as their temperature is increased since with the increased number of collisions of electrons their mean free paths are shortened. Also the crystalline structure of metals explains their ability to be reformed plastically. (Figure 26.) The lattice planes, bands can be dislocated with respect to one another but deformation as such, does not take place because the charge distribution in the metallic lattice is practically uniform, i.e.: it does not imply significant change in the length of the paths or in the forces acting. Although, in case of ionic crystals, considerable deformations are observable as a result of lattice plane dislocation. That also is the explanation for out of all the crystalline materials the metals being the most plastic. The same explains the outstanding flexibility.
The high density of metals is coming from the grid members being rather tightly packed. (In case of low density metals the nuclear radius is the key as low density is caused by a larger nuclear radius and a low mass number)

**Week 4 Video session:**

https://www.youtube.com/watch?v=GipNmLZUnRc

https://www.youtube.com/watch?v=G45T6D6K_GY

https://www.youtube.com/watch?v=OpKxyeU2dc0

**Week 4 Question session:**

Define latticework, lattice constant, lattice energy, unit cell, and dislocation.

*Essay:* Lattice types comparison and contrast

*Essay:* The Band Theory
Week 5: Phase-based classification and characterization of material systems. Formation of crystalline solid bodies. Glassy and macromolecular materials.
Macroscopic crystalline bodies

Formation of crystalline solid bodies

The macroscopic solid bodies including the metals in general are not monocrystalline but consist of a sub-microscopic mosaic-like set of crystal grains (crystallites). The initially, randomly-oriented internal crystal structured grains individually growing around the so-called crystallisation centres get into contact with each other during solidification. The location and size of these grains with special respect to each other defines the fabric, the texture of the crystal. (Figure 27.)

Factors influencing the crystallisation

The metals crystallise from melts; the high viscosity of the melt prevents the development of the crystals, consequently no regular face surfaces are formed unlike in case of the solid matters crystallised from melts. The texture of the crystals is dependent on the temperature. The cement, for instance, solidifies slowly in cold, but long crystal Calcium-silicate-hydrates are formed within providing enhanced structural strength; while under warmer circumstances short crystal reaction products are created with less strength. The fabric is also determined by speed of cooling. Figure 28. shows the vertical and horizontal cross-sections of a solidified steel ingot. Where the speed of heat absorption is the greatest, a zone of small crystals is formed.(1). Where heat is removed at a slower pace, practically changing linearly by distance, a zone of large long-crystals is found.(2), while in the middle the formation of crystals is uniform.(3).
Crystallographic defects

The perfect crystal in which atoms, ions and molecules are located in strict order, is only an idealistic case. The real crystals are not of uniform built up. Any kind of deviation from the perfect crystal is called a stacking fault or crystallographic defect. Inside the crystal the atoms are not all exactly in the same energy state. Under given circumstances, one of the atoms situated close to the surface can gain such a large amount of energy that it makes it to the surface while its original place becomes an opening, a so-called vacancy.

If the geometric environment allows it and the temperature is high enough the atom may migrate back to a place amongst the other atoms. That is called penetration. Own or foreign atom can penetrate alike. If a foreign atom is there in the grid corner (ion or molecule) instead of the one supposed to be there, we speak about substitution. These defects are the point defects (Figure 29.)

The distortion of the dimensions of the elementary cell can even take place upon crystal formation. These are the linear defects (dislocations) (Figure 30.)
The planar- and spatial defects are caused by disorder appearing at grain edges, pores and voids inside the material. (Figure 31.)

1) crystal grain
2) crystal grain with solid, liquid and gaseous voids
3) pore,
4) grain edge.

The defects occurring in a crystalline material can significantly influence a number of its macroscopic properties such as the mechanical properties the tendency to corrode, etc.

Figure 31.: Planar and spatial defects in crystalline material [4][22]

2.3.2. Glassy materials

The glass is such an inorganic melt that cooled down and solidified without observable crystallization. The glassy materials can be regarded as overcooled (super cooled) liquids in which high viscosity prevents the formation of regular lattice. Their structure is similar to that of the Silicates (Figure 20.) but the network is somewhat distorted in comparison to crystalline quartz.

Figure 32.)Uniform, tetrahedral lattice quartz (SiO₂).

The part b) of the figure depicts a silicate glass, where it is visible that in spite of the identity of the constitutive atoms, the ‘rings’ are significantly distorted. The irregularity increases even more in case of the Natron glass (part c of the Figure): The penetration of the Sodium results open ‘rings’. The glassy state is a metastable one in which the internal energy and volume of the material is larger than as if it was in crystalline state. Under specific circumstances the crystallisation can even take place (getting dull).
The melting procedure of the glassy materials does not take place at a specific temperature but is ongoing through a wide interval of temperature (yielding region). Because of the distortion of the structure the strength of the bonds is not uniform therefore the melting is not synchronised.

To the production of a common glass $\text{SiO}_2$ (silica sand), $\text{CaCO}_3$ (limestone) and $\text{Na}_2\text{CO}_3$ (Sodium-Carbonate//Soda//) is used. In between them the following reaction takes place in melt state:

$$\text{Na}_2\text{CO}_3 + \text{CaCO}_3 + 6 \text{SiO}_2 \rightarrow \text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2 + 2\text{CO}_2$$

Out of the oxides listed above the Silicon-dioxide is the network forming; the Calcium-dioxide is the stabiliser, while the Sodium-oxide being the smelter.

### 2.3.3. Macromolecular matters

The majority of the macromolecular materials do not even possess a distorted crystal structure introduced at glassy materials, therefore to this group of materials the *amorphous* (structureless) denotation is used. The constitutive compounds building up the macromolecules are bonded together covalently often into a rather large, 40000-300000 relative molecular mass formations.

**Natural macromolecular materials**

*Rubber:* It is produced from the milk sap (latex) of the rubber tree (*seringa*). The latex is rich in *isoprene*, can be polymerised into raw caoutchouc (India-rubber), having added Sulphur to it, the outcome is rubber. Its dark colour is caused by the soot.

*Cellulose based:* cellulose nitrate: flammable (celluloid, fumeless gunpowder)
Cellulose acetate: not flammable (filmstrip)
Viscose: wood pulp dissolved in NaOH and CS₂ (rayon, cellophane)

India-rubber:
Natural rubber, also called India rubber or caoutchouc, as initially produced, consists of polymers of the organic compound isoprene, with minor impurities of other organic compounds plus water. Malaysia is a leading producer of rubber. Forms of polyisoprene that are used as natural rubbers are classified as elastomers. Natural rubber is used by many manufacturing companies for the production of rubber products. Currently, rubber is harvested mainly in the form of the latex from certain trees. The latex is a sticky, milky colloid drawn off by making incisions into the bark and collecting the fluid in vessels in a process called “tapping”. The latex then is refined into rubber ready for commercial processing. Natural rubber is used extensively in many applications and products, either alone or in combination with other materials. In most of its useful forms, it has a large stretch ratio and high resilience, and is extremely waterproof. (https://en.wikipedia.org/wiki/Natural_rubber)

Artificial macromolecular materials: polymers

Polymers are gained from monomers. The monomers are organic compounds containing at least two reactive (bi-functional) groups through which the monomers can have C-C, C-N, C-O, etc. type of chemical bonds with each other.

n x monomer → polymer
n=thousands
n x monomer → oligomer
n=few
various monomers → copolymer

A). Macromolecular polymers manufactured with polymerisation

From unsaturated, incomplete monomers with the tearing up of the double bond, without by-products whatsoever, macromolecular polymers are created. The launching procedure requires activating energy that is made up for by heat or by chemical tools, namely chain termination inhibitors.

General formula: nA → (A)n

Examples:

\[
\begin{align*}
nCH_2=CH_2 & \rightarrow -[CH_2-CH_2]_n \\
\text{ethylene} & \quad \text{polyethylene (PE)} \\
nCH_2=CH & \rightarrow -[CH_2-CH]_n- \\
\quad \bigg| \quad \bigg| \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{propylene} & \quad \text{polypropylene (PP)}
\end{align*}
\]
nCH₂=CH → [CH₂-CH]ₙ⁻
\[
\begin{array}{c}
\text{Cl} \\
\text{vinyl-chloride}
\end{array}
\quad \text{Cl}
\]
\quad \text{polyvinyl-chloride (PVC)}

n(CF₂=CF₂) → [CF₂-CF₂]ₙ
\[
\begin{array}{c}
\text{tetrafluoroethylene} \\
\text{teflon}
\end{array}
\quad \text{poly-vinyl-benzene (polystyrene, PS)}

poly-methyl-methacrylate (Plexiglass, PMMA)

artificial caoutchouc etc.

**B) Macromolecular materials via polycondensation**

The interconnection of the monomer molecules is always followed by the ejection of a small molecule by-product of some kind; generally water is secreted.

General formula:

\[
x-R-y + x-R'-y \rightarrow x-R-R'-y+xy \\
\downarrow \quad \downarrow \\
\text{dimer} \quad \text{e.g.: } H₂O
\]

\[
x-R-R'-y + x-R-y \rightarrow x-R-R'-R'-y+xy \\
\downarrow \\
\text{trimer......}
\]

Examples:

Phenoplasts (Phenol+methanol→→Bakelite)

Polyamides, aminoplasts, poly esters, silicones, etc.

**C) Macromolecular materials via polyaddition**

The polyaddition generally can be written up as: nA + nB → (AB)ₙ.

Examples: epoxy resin (pl. polymer concrete)

polyurethane (PU, e.g.: paint, polish, foam)
Bonding possibilities:

The bond between macromolecules can be of various kinds. The chemical bonds are shown by Figure 34, in part 2 and 3, where Sulphur atoms or Hydrogen bridges establish inter chain or end-of-the chain connections. The polymers connected by chemical bonds are hardened upon heat effect (e.g.: vulcanisation of rubber).

Figure 34. part 4, 5 and 6 depict a physical connection: interlocking, an interaction of chains located close to one another and the penetration of a solid matter, for instance, soot. The physical bonds are weakened or destroyed by heat effect (e.g.: PVC thermoplastics)

![Figure 34: The bonding possibilities of linear macromolecules [4]](image)

The behaviour of polymers regarding heat effects is characterised by the thermo-mechanic curve (Figure 35.)

On the curve the three physical states of polymers can be very well disentangled ranging from glassy through highly elastic to viscous. The interstate circumstances are defined by the \((T_d)\) solidification and \((T_I)\) yielding regions. Not all polymers have all the three states. Polymers having a small degree of polymerisation are either glassy or viscous exclusively. Higher the degree of polymerisation (the number of monomers) wider the elastic region.
Figure 35.: Thermo-mechanical curve of polymers [4]

**Week 5 Video session:**

https://www.youtube.com/watch?v=kr46wPjfz7U

https://www.youtube.com/watch?v=4NZV0ZvDm5c

https://www.youtube.com/watch?v=CKq42J7SaWw

**Week 5 Question session:**

Describe the formation of the crystalline solid bodies.

*Essay: Macromolecular materials and bonding.*

Define ingot, vacancy, penetration, substitution, point and line defects, glassy and macromolecular.
Week 6: Characterisation of homogenous material systems. Mixtures, solutions
3. Categorisation of material systems by particle size and dispersion

Homogeneous (uniform) material systems:
- Pure materials: elements and compounds
- Mixtures (solutions)

Heterogeneous (non-uniform) material systems: mixtures

3.1. Homogeneous material systems

In homogeneous systems there are no macroscopic boundaries. The homogeneous systems consist of a single phase. The size of the particles is less than $10^{-9}$ m (1 nanometre) and the composition of the set is unvaried at all parts of the system. They may be of single- or multi-components as well.

*Single component systems:* pure materials (element, compound) containing only one type of component (atom, ion pair, molecule).

*Multi-component systems:* mixtures containing many constituents.

Example being the gas mixture of air.

- Liquid mixtures (mixture of ethanol and water)
- Gas-liquid mixture ($O_2$ or $CO_2$ aqueous solution)
- A solid-liquid mixture (aqueous solution of NaCl)
- Solid-solid mixtures (homogeneous alloys)

Mixtures or solutions may be *ideal:* in this case no thermal effect takes place by mixing the components furthermore; the volume of the mixture is the sum of the volume of the components respectively in pure form. Reason being: interactions within the molecules of the pure components are practically of the same strength as the interactions between the molecules of the two components. In case of real mixtures or solutions, thermal effects do occur by mixing the components together. The total volume this time around will not be equal to the sum of the volumes of the components in pure form. (e.g.: 20 cm$^3$ of Sulphuric acid+80 cm$^3$ of water=98 cm$^3$ mixture). If the volume increases, we are talking about dilatation, if reduced, we call it contraction. The change is caused by the intermolecular forces of the two components in the interaction being smaller or bigger than between molecules of substances respectively.

**Mixtures, solutions**

They can be in gaseous, solid or liquid state. Those mixtures in which one component is disentangled from the rest for having a role important from a practical point of view are called *solutions.* The latter may be in liquid or solid state. The component playing a unique role is the *solvent,* which can be mixture itself as well.

In addition to the previously discussed status indicators (P, R, T) the knowledge of the composition of the mixture (concentration) is necessary for characterization as well.

This can be specified in several ways.
a) Percentage Composition:
- Volume %: How many cm³ of dissolved substance there are in 100 cm³ of solution
- Mixed %: How many grams of dissolved material there are in 100 cm³ of solution
- Mass %: The number of grams of dissolved material in 100 g of solution.

b) 1 dm³ (1 L) regarding solution volume:
- g/dm³: The number of grams of solutes found in 1 dm³ of solution
- 1 mol/dm³ = 1 M solution: How many molecular mass of solutes there are in 1 dm³ of solution

**Solubility of gases in liquids**

Henry and Dalton's Law: \( C = k \cdot p \)

where

- \( a \) - saturation concentration
- \( k \) – constant, depending on the quality of the gas and that of the solvent at a given \( T \)
- \( p \) - gas pressure (partial pressure of gas)

Bigger the pressure and lower the temperature, higher the solubility. In case of melts of metal, solubility of gases is increased by temperature (gases may dissolve atomically or in an ionic way there). If a chemical bond is also formed, solubility is particularly good, such as in case of hydrochloric acid dissolved in water:

\[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \]

The third component is of salt-fallout-creating nature i.e. reduces the solubility of the gas. Sugar reduces the solubility of Carbon-dioxide in water and Sodium-Chloride has the same effect on Oxygen.

**Dissolution of solids in liquids**

Dissolution process continues until the state of balance between solid (crystal) and liquid phase is reached. In this case the solution is saturated. The solubility is a respective feature varying from material to material. This variation of solubility depends on the material quality, the temperature, and slightly on the pressure. Higher temperature usually enhances solubility, but for instance in case of the Calcium-hydroxide (\( \text{Ca(OH)}_2 \)) it has solubility decreasing effects. During the dissolution, a saturated solution layer is formed around the solid particles, from which solute elements get to the unsaturated solution parts by diffusion.

The followings can increase the rate of dissolution:
- Mixing (stirring)
- Reduction of grain size of the solid i.e. increasing the surface area:

The surface area is measured in: \( \frac{m^2}{kg} \); \( \frac{m^2}{m^2} \)
Upon the solutions cooled down (where by T, solubility is increased) the precipitation of crystals begins. Sometimes *supersaturation* (oversaturation) can take place (metastable state), but by shaking or by *inoculation* with crystals of the solute, crystallization begins that is the solid began to precipitate.

**Hydration, solvation**

Empirical observation being: "similar dissolves in similar", namely, polar covalent compounds dissolve in polar materials, covalent compounds in covalent solvents. The thermal energy alone is not enough to set ions free and disintegrate the crystal lattice into free ions since the dissolution in the majority of the cases takes place even at low temperature. The extra energy is gained from the *interaction* of ions and solvent molecules. In case of water, hydration interaction, in case of other solvents solvation interaction is there. **Figure 36.** NaCl crystal dissolution in water. Dipole water molecules in proper orientation surround the Sodium and Chloride ions. The hence developed hydration interaction is sufficient enough to rip off ions from the otherwise fairly strong ionic grid with the help of water molecules. Surrounded by water molecules, there are hydrated ions in the solution

\[
\text{NaCl} + \text{water} \rightarrow \text{Na}^{+}_{\text{aq}} + \text{Cl}^{-}_{\text{aq}}
\]

where \( \text{aq} = \text{aqua (water)} \)

![NaCl crystal structure](image1)

*Figure 36.* Dissolution of ionic lattice crystal (e.g.: NaCl) in water [3]

**Laws in dilute solutions**

Empirical fact is that dilute solutions’ freezing point is lower, boiling point is higher than that of pure solvents. The extent of change is proportional to the concentration. If in a clear solvent a non-volatile material is dissolved the solvent’s original vapour pressure is always
reduced. **Figure 37.** Part a) shows the developed state in case of pure solvent. The light circles represent the molecules of the solvent. Part b) refers to the solution where the dark circles represent molecules surrounded by the solvent. The amount of free solvent molecules in the solution became relatively less; much like that of those that made it to the vapour space moreover, the vapour pressure decreased at a given temperature.

![Figure 37: Vapour pressure of a pure solvent and solution [4]](image1)

**Figure 38.:** Temperature dependence of the vapour pressure of a solution and a pure solvent [4]
The vapour pressure of the solution, if a non-volatile component is dissolved, is always less than that of the pure solvent. (Figure 38.) The (p) -T vapour pressure curve of the solution therefore always passes under that of the pure solvent. The solution also has a higher boiling point ($\Delta T_{fpem}$) than the solvent since boiling occurs when the saturated vapour pressure reaches the atmospheric pressure. In case of a dilute solution (where only the solvent freezes) the freezing point will be lower than the pure solvent’s freezing point. Since the freezing point of a solution is the very temperature at which the solid and liquid phase vapour pressure is the same, freezing point decrement ($\Delta T_{fpcs}$) takes place as shown in the figure.

**Dissolution of liquids in liquids**

The solubility of liquids with one another depends on the material quality and the temperature. The Ethyl alcohol and the water mixes unlimitedly, while the hydrocarbons and the water practically do not mix in each other. Water and ether have a limited solubility. 

**Figure 39.** shows the temperature dependence of the solubility of material A and B relative to one another. The area inside the curve is of heterogeneous nature, while the area outside being homogeneous. The systems at hand do not mix. By raising the temperature solubility usually increases. Above the temperature of $T_{kr}$ mixing becomes unlimited, the heterogeneous system homogeneous.

**Solid mixtures**

May be created upon cooling of metallic melts:
- Ionic-bound chemical compounds
- Metallic, so-called *intermetallic* compounds
- Solid solutions (homogeneous alloys)
- Heterogeneous Alloys
**Intermetallic compounds:**

Materials composed of two or more types of metal atoms, which exist as homogeneous, composite substances and differ discontinuously in structure from that of the constituent metals. They are also called, preferably, intermetallic phases. Their properties cannot be transformed continuously into those of their constituents by changes of composition alone, and they form distinct crystalline species separated by phase boundaries from their metallic components and mixed crystals of these components; it is generally not possible to establish formulas for intermetallic compounds on the sole basis of analytical data, so formulas are determined in conjunction with crystallographic structural information. ([http://encyclopedia2.thefreedictionary.com/Intermetallic+Compounds](http://encyclopedia2.thefreedictionary.com/Intermetallic+Compounds))

In solid solutions, one of the substances is dissolved in the crystal lattice of the other material. The latter is considered to be the solvent. If the solid solution is formed out of two elements, that are having significantly different atomic radii, such as Carbon and Iron, then penetration solid solution is created. The atom of the smaller diameter can occupy the space between larger atoms without sustaining any kind of distortion whatsoever. ([Figure 40. b](#)) A distinctive feature being of the penetration solid solutions that the solute can easily move around in the space between the larger solvent atoms i.e.: the rate of diffusion is enhanced. For instance, at heat treatment of steel the aforementioned phenomenon is of utmost importance. The chemical nature and size of the components of the substitutional solid solutions are similar, to those found in pure elements as well as the interactions being completely ordinary. Gold and Silver form such alloys with one another in various ratios. ([Figure 40. c](#)) Penetration and substitution can take place simultaneously. ([Figure 40. d](#)) If one component of the alloy is at present in such an amount that makes dissolution impossible, a heterogeneous alloy takes shape.

![Figure 40.: Solid solution formation possibilities](#)
Week 6 Video session:

https://www.youtube.com/watch?v=RqSr45MB7M

https://www.youtube.com/watch?v=gxmpr09Xk4Y

https://www.youtube.com/watch?v=re9r0kzQp_M

Week 6 Question session:

Essay: Dissolution of solids in liquids

Describe the laws of dissolution regarding dilute solutions.

Give the definition of ideal solutions, solvation, oversaturated, inoculation, vapour space, vapour pressure, and intermetallic.
Week 7: Characterisation and classification of heterogeneous material systems. Phase diagrams
3.2. Heterogeneous material systems

Heterogeneous systems consist of several phases that are separated by macroscopic interfaces. The size of the dispersed particles is bigger than \(10^{-9}\) m (1 nm).

Depending on the size of the dispersed particles we distinguish:
- Macro heterogenic or coarse disperse systems (particle size greater than 500 nm)
- Micro heterogenic or colloidal disperse systems (particle sizes from 1 to 500 nm)

New surface interface elements can be created by increasing the surface area. (Figure 41.)

The most common methods are: deformation (laminar or fibril deformations form the deform systems), dispersion (disperse systems produced by chopping), condensation (Crystallization, condensation, fume, etc.).

![Diagram](image)

**Figure 41.** Illustrates deformation and dispersion [24]

In Table 3, the surface and the surface energy change is shown in case of chopping a 1 cm cube.

<table>
<thead>
<tr>
<th>Edge length</th>
<th>Number of cubes</th>
<th>Total surface area</th>
<th>Surface energy [J]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 cm</td>
<td>1</td>
<td>6 cm(^2)</td>
<td>4.6*10(^{-3})</td>
</tr>
<tr>
<td>1 mm</td>
<td>10(^3)</td>
<td>60 cm(^2)</td>
<td>4.6*10(^{-4})</td>
</tr>
<tr>
<td>1 μm</td>
<td>10(^{12})</td>
<td>6 m(^2)</td>
<td>4.6*10(^{-1})</td>
</tr>
<tr>
<td>1 nm</td>
<td>10(^{21})</td>
<td>6000 m(^2)</td>
<td>460</td>
</tr>
</tbody>
</table>

**Table 3:** Surface area and surface energy in the function of choppiness [4]

The disperse systems are composed of two parts: a homogeneous dispersing medium and the dispersed material within it. Both may be gas, liquid and solid. The most common method of classification is shown in Table 4.
Table 4.: Disperse system classification [4]

<table>
<thead>
<tr>
<th>Dispersing medium (phase) bedding medium</th>
<th>Dispersed part (phase) Embedded material</th>
<th>Name of the system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Liquid</td>
<td>Aerosol (fog, cloud)</td>
</tr>
<tr>
<td>Gas</td>
<td>Solid</td>
<td>Solid aerosol (fume, dust)</td>
</tr>
<tr>
<td>Liquid</td>
<td>Gas</td>
<td>Gas-dispersions, foams (foam of detergents, fire fighting foams)</td>
</tr>
<tr>
<td>Liquid</td>
<td>Liquid</td>
<td>emulsions (milk, mineral oil)</td>
</tr>
<tr>
<td>Liquid</td>
<td>Solid</td>
<td>Suspensions, (aero)sols, (pug, clayey water)</td>
</tr>
<tr>
<td>Solid</td>
<td>Gas</td>
<td>Solid foams (dry concrete, pumice)</td>
</tr>
<tr>
<td>Solid</td>
<td>Liquid</td>
<td>Solid emulsions, gels (wet concrete, ivy((amber))</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid</td>
<td>Heterogeneous alloys (metal alloys, glasses, inclusions)</td>
</tr>
</tbody>
</table>

Figure 42. illustrates the two typical types of emulsions. In systems such as the w/o system, drops of water are dispersed in oil, while in case of the o/w systems oil droplets are observable in water.

Surfactants:

are compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants.(https://en.wikipedia.org/wiki/Surfactant)

3.3. Equilibrium conditions in heterogeneous systems. Phase Law

Phase diagrams very well depict the status changes, the preconditions of the interlocking phases and crystalline modifications and the intervals of p, V, T, of heterogeneous systems consisting of two or more phases.

Gibbs phase rule is valid to heterogeneous phases in equilibrium with no chemical reaction taking place within:

\[ f + sz = k + 2 \]

where \( f \) - the number of phases in equilibrium
sz - the number of degree of freedom (the number of indicators that under certain circumstances may be modified freely within certain limits without having the number of phases changed)
k - the components (those components that are strictly necessary for the construction of such heterogeneous systems so that their masses shall be present in arbitrary proportions.)

The status indicators of chemically uniform substances are the pressure, the temperature and the volume, from which only two being independent of one another. In case of multi-compound systems the concentration values are considered independent status indicators as well. In case of water and water vapour in balance with the aforementioned, the number of components is one while the number of phases is two.

In the equilibrium (reversible) process of the limestone decomposition and lime solidification:

\[ \text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2 \]

The system is of three phases however, the number of components being two as with the help of any two of the materials the third can be created.

**Phase diagram of single-component systems**

The water phase diagram is shown in **Figure 43.**

In the region of Water (also ice and vapour):

\( k = 1 \) (H\(_2\)O)
\( f = 1 \) (water)
\( sz = 2 \) (P and T freely variable within the range)

along the line A-0 (ice-vapour equilibrium, similarly to Line 0-B and 0-R):

\( k = 1 \) (H\(_2\)O)
\( f = 2 \) (ice and vapour)
\( c = 1 \) (or T, P or variable)

At the point 0: \( k = 1 \) (H\(_2\)O) \( f = 3 \) (ice, water and steam) \( \text{No} = 0 \)

![Figure 43: The phase diagram of water [4][26]](image-url)
The 0 point of the phase diagram, the so-called triple point can be reached only in a closed system and it is not identical to the freezing point of the water. In case of the latter, two phases—water and ice—are present and the pressure is 102000 Pa.

SiO$_2$ is also a one-component system with various known different crystalline modifications. The Fenner chart shows the stable modifications regarding to different temperature ranges. (Figure 44.)

![Figure 44: The phase diagram of SiO$_2$ [27]](image)

The modification change occurring at 573 °C ($\alpha$ quartz $\rightarrow$ $\beta$ quartz) is fast, other transitions are slow. Upon production of glass the cooling of the quartz melt is relatively quick and stable modifications are not formed according to Figure 43., therefore the glass is in a metastable state. (Figure 45.) The SiO$_2$ modification changes come alongside with volume changes ($\beta$ $\rightarrow$...
In case of metals and metal alloys, out of the status indicators pressure can be omitted, consequently the phase law is modified as follows:

\[ f + sz = k + 1 \]

**Figure 46.** illustrates the effect of modification changes upon cooling and heating iron. On the horizontal segments of the cooling (and heating) curve (at 1536 °C, the melting point of iron, at 1392 °C the iron δ iron – γ at iron modification change, etc) under the term of the phase law:

- \( k = 1 \) (Fe)
- \( f = 2 \) (at 1536 °C: a melt and δ iron, at 1,392 °C δ iron and γ-iron)
- \( sz = 0 \)

On the ascending and descending sections:
- \( k = 1 \) (Fe)
- \( f = 1 \) (above 1536 °C a melt,
  Between 1536 and 1392 °C δ Iron)
- \( c = 1 \) (T may vary on a given section)
Phase diagram of two-component systems
(The components do not form a compound)

Figure 47. Phase diagram of systems consisting of salt and water [4][31]

Figure 47. depicts the phase diagram of systems built up of salt and water. The vertical axis is the temperature; the horizontal axis is the concentration. A stands for the freezing/melting point of pure salt, B stands for that of pure water. If salt is added to the water in increasing amounts the melting point of the solution is decreased along the BE line. At point E, the solution becomes saturated. The AE curve shows the effect of the water given to the salt in increasing amounts. By cooling the $x_1$ consistency, unsaturated solution, as AE line is reached, salt is precipitated. In case of the $x_2$ consistency, ice is formed as BE curve is reached. When cooling the E consistency solution, at the temperature corresponding to point E, a mixture consisting of ice and salt crystals, eutectic precipitates. The eutectic consistency and the eutectic temperature are dependent on the material qualities of the components. If salt and ice is mixed with an appropriate ratio regarding the eutectic consistency, then the system temperature falls to the temperature value corresponding to the eutectic temperature. In this case salt dissolves in the molten water on the surface of the ice but this saturated solution however, is not in balance with a 0 °C melting ice, therefore to dilute the solution the ice begins to melt withdrawing heat from the surrounding ambience. The cooling lasts as long as the temperature of the mixture reaches the eutectic temperature. Refrigerant mixture (cryogen) production and de-icing of roads work on the same principals. (The temperature of the mix of the finely crushed ice and salt could drop to -22 °C maximum).

Figure 48. shows the cooling curves and phase diagram construction in case of two-component, heterogeneous systems.
Figure 48.: Construction of phase diagram [32]

**Week 7 Video session:**

https://www.youtube.com/watch?v=h5dwpTgacqc

https://www.youtube.com/watch?v=2a_OYiAC7_s

https://www.youtube.com/watch?v=XEbMHmDhq2I

**Week 7 Question session:**

*Essay: Phase Law*

*Essay: Phase diagram construction*

Define the following terms: disperse system, condensation, surfactant and eutectic consistency.
Week 8: Phenomena on the interfaces. Stabilisation, dissipation of disperse systems
3.4. Interfacial phenomena

The forces acting on the atoms at the boundary of two phases are not identical to the forces within the phases since outwards only the unoccupied forces act. The energy appearing on the interface, usually higher than the average energy of the phase, is called the *interfacial energy*. Therefore the total energy of the body system is comprised of the components:

\[ E_t = E_b + E_f \]

The energy of the constitutive elements of the body system (atoms, ions, molecules) the internal *energy* \( E_b \) is proportional to the mass of the body and its volume while the *surface energy* \( E_f \) is proportional to the surface area of the body, the number of edges, nodes and voids.

**Surface tension of liquids**

The forces acting on the interface inwards push the molecules to each other. Therefore when we are to enlarge the surface, we carry out work against these aforementioned forces pushing the molecules next to one another. This force inducing the contraction is called *surface tension*. (Unit: N/m).

The surface tension (\( \gamma \)) decides the size of the drop of liquid that is leaking out slowly through a capillary (\( r = 0.1-0.3 \text{ mm} \)). The detachment of the drop is hindered by the surface tension action on the very edge of a pipe. At the moment of detachment:

\[ mg = 2 \pi r \gamma \]

The surface tension of some liquids (10\(^{-3}\) N/m):

- Water: 73 (18 °C)
- Glycerol: 20 (66.6 °C)
- Benzene: 20 (29 °C)
- Ethyl-alcohol: 20 (22 °C)

**Temperature dependence of the surface tension**

The change of surface tension with respect to the temperature is described by the Eötvös rule:

\[ \gamma Vm^{2/3} = k (T_{kr} - 6 - T) \]
where

\[ T \quad \text{actual temperature} \]
\[ T_{kr} \quad \text{Critical temperature} \]
\[ V_m \quad \text{Molar volume} \]
\[ k \quad \text{Eötvös constant} \]

If \( T = T_{kr} - 6 \), the surface tension becomes zero.

\( \gamma V_m^{2/3} \) means the work required to form a molar surface.

The Eötvös constant to a normal liquid is: \( 2,1 \cdot 10^{-7} \) JK\(^{-1}\)mol\(^{-2/3}\)

Eotvos rule:

The Eötvös rule, named after the Hungarian physicist Loránd (Roland) Eötvös (1848–1919) enables the prediction of the surface tension of an arbitrary liquid pure substance at all temperatures. The density, molar mass and the critical temperature of the liquid have to be known. At the critical point the surface tension is zero. ([https://en.wikipedia.org/wiki/E%C3%B6tv%C3%B6s_rule](https://en.wikipedia.org/wiki/E%C3%B6tv%C3%B6s_rule))

If \( k < 2,1 \cdot 10^{-7} \), that means that there are parts stuck together (associates) in the liquid i.e.: it has a structure. Such liquid is the water, for instance.

If \( k > 2,1 \cdot 10^{-7} \), then the molecules are standing oriented on the surface of the liquid. This way they occupy fewer surface than as though they were spheres therefore the energy of the surface is changed.

e.g.: butyl - alcohol, carboxylic acids (polar covalent molecules)

This phenomenon occurs, in the solution of groups of long Carbon chain molecules having covalent groups within, as well.

**Capillary active and capillary inactive materials**

If the concentration of a material on the surface of a liquid is increased or decreased, we speak about positive or negative adsorption. The former decreases, while the latter increases the stresses. Those materials that are capable of changing the surface tension significantly are called capillary active materials (surfactants) while those unable or just able to do so to a small extent are called capillary inactive materials. ([Figure 49.](#))

Regarding water

Capillary active materials: organic compounds, alcohols, soaps (surfactants)
Capillary inactive materials: electrolytes, strongly polar compounds e.g.: sugars

![Figure 49.: The change of the surface tension of water in the function of the quantity of electrolytes and surfactants](image-url)
Moisturising

Dropping a drop of liquid onto a solid surface the outcome could be any of the following three:

a) The liquid sprawls (is spread) uniformly. This is the case of the total moisturizing and its reason being the interaction of the solid and liquid molecules is stronger than that of between liquid molecules. The wetting angle or contact angle: $\theta \approx 0^\circ$

b) We speak about partial moisturizing if the shape of the liquid is lens-like. $0^\circ < \theta < 90^\circ$

c) Sphere shaped drop. There is practically no moisturising. $180^\circ < \theta < 90^\circ$

In case of partial sprawl, three types of interfacial stresses are to be taken into account. The interfacial stresses are force type of quantities, consequently can be represented by vectors.

In equilibrium state the shape of the drop is unchanged and the following correlation can be written up:

$$\gamma_{sz} = \gamma_{fsz} + \gamma_{fl} \cos \theta = \gamma'$$

where $\gamma'$ a $\gamma_{fl}$ and $\gamma_{fsz}$ are the projections of the resultants of the vectors.

Changing the interfacial stresses, the shape of the drop can be influenced i.e.: the moisturising. The liquids of small surface tensions (benzene, oils, etc.) moisture better any solid surface than the water. Water moisture fairly good the glass and various minerals.
Detergency

Because of the above mentioned circumstances, the oil cannot be washed from a solid surface by with water. If with appropriate capillary active materials (for instance, detergents), the surface tension of the water is decreased, the contamination is removable now that the detergent moisturises.

Disperse systems important from practical point of view

Dispersed particles in a dispersion medium possess surface areas consequently there is adhesion between them. As time goes on, the disperse system may cease to exist, due to the:
- Aggregation of the solid particles
- Coagulation of the liquid particles.

The dissipation of the system is signed by settlement or decantation depending on whether the disperse part or the medium is the one having higher density.

In many cases it is necessary to stabilise the disperse systems, most frequently the emulsions, the suspensions, the foams.

Figure 50. showing the o/w (oil in water) and w/o (water in oil) type of emulsion stabilisation with capillary active materials. The polar part of the capillary active material (emulsifier), such as its Carboxyl group (-COOH) is adsorbed in both cases oriented towards the alike polar water. The apolar part (e.g.: alkyl chain) on the other hand, is directed toward the apolar oil. Eventually, such a boundary layer is formed, that serves as a transition between the dispersing medium and the dispersed particle that mechanically prevents the aggregation and coagulation of particles as well.

The appropriate electrolytes are adsorbed on the surfaces of the dispersed particles (either the cations or the anions). As a result of this, the particles having the same surface charge repulse each other, that provides the system with stability. On occasion, even the suspensions can be stabilised with coarse particles adsorbed.
In practice, the dissipation of disperse systems (fumes, emulsions, suspensions) is necessary rather often. The issue at hand can be approached in a number of different ways.

**Isolation of the disperse part by settling:**
- based on the density differences of the phases, the procedure can be influenced by changing the viscosity of the medium.
- centrifuge

Filtration: The pre-condition of the method being that the medium moistures the sieve more than the dispersed particles would

**Coagulation** (emulsions)

The abolition of the effect of the boundary layer (capillary active material) providing the stability (demulsification) – is a special and frequent task.

**Electrophoresis**

Parts stabilised with surface charges placed in an electric environment will move (the cations towards the negative cathodes, the anions into the direction of positive anodes), as a result of which the two phases are separated.

---

**Week 8 Video session:**

https://www.youtube.com/watch?v=-jftkF5e6jY

https://www.youtube.com/watch?v=djIzXvwIz5U

https://www.youtube.com/watch?v=f--8eT4wt5Q

**Week 8 Question session:**

Define interfacial, surface energies, adsorption, moisturising, coagulation and sprawl.

State and explain the Eötvös rule.

Describe the methods of isolation of disperse systems.
Week 9: Chemical reactions
4. Chemical reactions

Those processes that imply the change of the chemical composition and structure of various materials followed by a change in energy of the order of magnitude of 40-400 kJ/mol are called chemical transformations or chemical reactions (dissolution, secession, changes of state (phase) or any process of chemical nature implying energy change).

(In chemistry the most important unit of substances is the mol. It is the measurement of a material system that contains as many elementary particles (electron, proton, atom, ion, and molecule) as many atoms can be found in 12.000 Gramm of mass number 12 Carbon isotope. There are 6.023·10^{23} particles in 1 mol of material.)

The chemical transformations are depicted with reaction equations. On the left hand side there are the interacting, on the right hand side, the formulas of the newly formed materials can be found. The reaction formulas can be regarded as material (mass) balance statements as well since the atomic symbols and chemical formulas stand for the molar quantities. Also, on the basis of the formulas the so-called stoichiometric computations can be carried out.

Example:

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]

100.09 g = 56.08 g + 44.01 g

Stoichiometry:

/ˌstoɪkiˈɒmɪtri/ is the calculation of relative quantities of reactants and products in chemical reactions. Stoichiometry is founded on the law of conservation of mass where the total mass of the reactants equals the total mass of the products leading to the insight that the relations among quantities of reactants and products typically form a ratio of positive integers. This means that if the amounts of the separate reactants are known, then the amount of the product can be calculated. Conversely, if one reactant has a known quantity and the quantity of product can be empirically determined, then the amount of the other reactants can also be calculated. (https://en.wikipedia.org/wiki/Stoichiometry)

4.1. The rate of chemical reactions

The rate or speed of a chemical reaction is the quantity of the transformed material over a given interval of time.

Factors influencing the rate of reactions

Concentration

In the A + B = C + D reaction to create C and D, A and D have to collide. At constant temperature, higher the concentration, higher the number of collisions will be.

The formation rate of C and D can be interpreted as: \( v = k [A][B] \)

Where \( k \) is the velocity constant (its value at constant temperature is independent of the concentration)

\[ [A] \text{ and } [B] \text{ are the concentration of the initial materials.} \]
In general case: \( n_1A + n_2B = m_1C + m_2D \), moreover \( v = k[A]^{n_1}[B]^{n_2} \)

**Temperature**

An increment in the temperature also increases the motion of the reaction partners hence the number of collisions.

**Activation energy**

The overwhelming majority of the chemical reactions only take place if there are molecular collisions and their energy is above average. **Figure 51.** shows the change of reaction heat and activation energy in case of processes implying heat release (exothermic) and heat absorption (endodermic).

![Diagram of exothermic and endothermic reactions](image)

**Exothermic reaction** | **Endothermic reaction**
---|---

The activation always means energy take-up and the source can be heat, light etc. The magnitude of the reaction is independent of the activation energy however, activation energy influences the rate of reaction as smaller the required energy, faster the reaction is to be.

**Catalysts**

The *catalysts* are such foreign materials that greatly enhance the rates of reactions without undergoing permanent changes themselves in the reaction as their participation is temporary. A comparatively small amount of them is generally adequate in comparison to the other reaction partners. The catalysed reaction is carried out in a different, lower activation energy way.
For instance: A + B ≠ AB without catalyst

In the presence of catalyst:

\[ A + \text{cat} \rightarrow [A\text{cat}]^* \]
\[ [A\text{cat}]^* + B \rightarrow AB + \text{cat} \]

**Specific surface area, grain size**

In case of heterogeneous phase reactions, smaller the grain size, larger the interface of the reaction partners and consequently faster the reaction.

**Mixing**

In case of heterogeneous phase reactions, mixing enhances the rate of reaction as it helps the ejection of the reaction by-products from the reaction zone. Without mixing only diffusion provides similar opportunities.

### 4.2. Types of chemical reactions

In what state (phase) are the participating materials in?

a) Homogenous reactions: The reaction partners are at present in the same state. They can be either in gaseous or in liquid phase.

b) Heterogeneous reactions: The reaction partners are in different phases, the chemical transformation takes place on the interface. It can be a gas-liquid, gas-solid, liquid-liquid (not mixing) or solid-solid type of reaction.

What is providing the energy necessary to the reaction?

- Heat – Thermal reaction
- Light – Photochemical reaction
- Radioactive radiation – radiochemical reaction
- Sound – acoustic chemical reaction

They can be catalysed of non-catalysed.

Formal classification:

a) *Unification*: (out of two or more matter a completely new matter is formed)

\[ \text{CaO} + \text{H}_2\text{O} = \text{Ca(OH)}_2 \]
\[ \text{C} + \text{O}_2 = \text{CO}_2 \]

b) *Decay*: Chemical bonds are destroyed meanwhile two or more particles are created.

Homolysis: \[ \text{Br}_2 \rightarrow 2\text{Br} \] (A covalent bonding pair is destroyed.)

Heterolysis: \[ \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \]
\[ \text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3^- \]
(Both electrons of the covalent bond remain in one of the decomposition products.)

**Dissociation:** a reversible decay

- Thermal dissociation (due to heat effect)
  
  \[ \text{CaSO}_4 \leftrightarrow \text{CaO} + \text{SO}_3 \]

- Electrolytic (As a result of solvation in electrolyte solution)
  
  \[ \text{MA} \leftrightarrow \text{M}^+ + \text{A}^- \text{ (generally)} \]
  
  \[ \text{NaOH} \leftrightarrow \text{OH}^- + \text{Na}^+ \text{ (in water)} \]

**Metathesis** (double decomposition) (unification and decay taking place simultaneously)

\[ \text{AB} + \text{CD} = \text{AD} + \text{BC} \]

\[ \text{Ca(OH)}_2 + \text{MgCl}_2 = \text{CaCl}_2 + \text{Mg(OH)}_2 \]

c) **Isomer** or intra-molecular transformation (a material of another structure is created)

**Based on reaction mechanism:**

a) **Simple reactions:** One step reaction of complete, saturated molecules. The activation energy is great since constant chemical bonds are needed to be destroyed.

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]

b) **Chain reactions:** Chain processes with the participation of free atoms and atom radicals. Usually the activation energy of the first, chain-igniting step is large while that of the subsequent steps is gradually decreasing as free atoms cease to take part.

- e.g.: HBr formation
  
  \[ \text{Br}_2 = 2\text{Br} \text{ (great activation energy – chain-igniting)} \]
  
  \[ \text{Br} + \text{H}_2 = \text{HBr} + \text{H} \text{ (chain-carrying)} \]
  
  \[ \text{H} + \text{Br}_2 = \text{HBr} + \text{Br} \text{ (chain-carrying)} \]
  
  \[ \text{H} + \text{HBr} = \text{H}_2 + \text{Br} \text{ (creates chain-carrying, but consumes as well)} \]
  
  \[ \text{Br} + \text{Br} = \text{Br} \text{ (snaps the chain – chain terminating)} \]

The chain reactions are usually of a high rate (e.g.: combustion, explosion)

c) **Ionic reactions:** Mainly take place in solutions where the solvent molecules enhance the creation of ions.

\[ \text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} \text{ (acid – base neutralisation reaction)} \]

\[ \text{NaCl} + \text{AgNO}_3 = \text{AgCl} + \text{NaNO}_3 \text{ (precipitation yielding reaction)} \]
**Week 9 Video session:**

https://www.youtube.com/watch?v=UL1jmJaUkaQ

https://www.youtube.com/watch?v=H6CRwdDft4U

https://www.youtube.com/watch?v=lU61WI1w63w

**Week 9 Question session:**

*Classify the reaction types on the basis of reaction mechanisms.*

*Essay: Activation energy and reactions involving change in heat*

*Define unification, decay, dissociation and metathesis.*
Week 10: Chemical equilibriums. The concept of pH. Hydrolysis of salts
5. The equilibrium of chemical reactions.

5.1. The Law of Mass Action

If a chemical reaction is reversible, ↔ usually it is marked with arrows.

\[ A + B \leftrightarrow C + D \]

A reversible reaction is never complete in any of the directions. Reaction rate can be written up to both reactions as:

\[ \rightarrow v_1 = k_1 [A] [B] \]
\[ \leftarrow v_2 = k_2 [C] [D] \]

Initially \( v_1 \) is high, then by the decrement of the concentration of the initial materials, it decreases. The concentration values of \( C \) and \( D \) are directly proportional to time; \( v_2 \) also performs some increment. In equilibrium, the speed of the two opposite processes is the same.

\[ v_1 = v_2 \]

\[ k_1 [A] [B] = K_2 [C] [D] \]

Since \( K_1 \) and \( K_2 \) velocity constants, at a constant temperature, are independent of the concentration the following can be written up:

\[ K = \frac{k_1}{k_2} = \frac{[C] [D]}{[A] [B]} \]

In general:

\[ n_1A + n_2B \leftrightarrow m_1C + m_2D \]

\[ K = \frac{[C]^{m_1} [D]^{m_2}}{[A]^{n_1} [B]^{n_2}} \]

This is the Law of Mass Action, \( K \) being the equilibrium constant.

Thus: In case of equilibrium the product of the equilibrium concentrations of the reaction products taken to the appropriate power divided by the product of the equilibrium concentrations of the initial materials taken to the appropriate power is a constant at constant temperature and pressure.

If the concentration of either of the materials is increased (adding) or decreased (subtracted from the system), the reaction takes another direction so that the value \( K \) remains constant.

According to the Le Chatelier – Braun principle.: if a system in equilibrium is exposed to some kind of external effect, the change taking place is such that it counteracts the external effects by mitigating the impact. (The system dodges the intervention) This is called the Least-constraint principle and it is valid all around in nature.

Le Chatelier-Braun principle:

the principle that if any change is imposed on a system that is in equilibrium then the system tends to adjust to a new equilibrium counteracting the change.

(http://www.thefreedictionary.com/Le+ChatelierBraun+principle)

A change of smaller or greater measure occurs in the equilibrium state of the system even when the volume, the temperature or the pressure is changed. Increasing the pressure moves
the system towards a decrement in volume. The equilibrium constant of the exothermic reactions is decreased with increasing temperature.

5.2. Protolysis processes
The dissociation of water, the concept of pH

The electrolytes in their solutions dissociate more or less to, ions (decay).

\[ \text{MA} \leftrightarrow \text{M}^+ + \text{A}^- \]

The law of mass action is also valid to equilibrium processes (\( K_d \) dissociation equilibrium constant):

\[ K_d = \frac{[M^+][A^-]}{[MA]} \]

It can be experimentally proved that the water also slightly dissociates:

\[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \] (\( 2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \))

\[ K_d = \frac{[H^+][OH^-]}{[\text{H}_2\text{O}]} \]

\( K_d \) can also be written up with the degree of dissociation:

\[ \alpha(\text{degree of dissociation}) = \frac{\text{Number of dissociated (decayed) molecules}}{\text{Total number of molecules}} \]

Denoting the concentrations with \( c \):

\[ K_d = \frac{\alpha \cdot c \cdot \alpha \cdot c}{(1 - \alpha) \cdot c} = \frac{\alpha^2 \cdot c}{1 - \alpha} \]

Based on measuring the conductivity of water it is safe to say that its degree of dissociation is extraordinarily low (at 25 °C 1.8 \( \cdot \) 10\(^{-9} \)), therefore its value in the denominator is negligible in comparison to 1. The water calibration concentration \( c = 55.5 \) since:

\[ \text{M}_{\text{water}} = 18 \text{ g} \]

\[ 1000 \text{ g} = \text{in} 1000 \text{ cm}^3 \text{ water} : c = \frac{1000}{18} = 55.5 \text{ mol/dm}^3 \]

\[ K_d = (1.8 \cdot 10^{-9})^2 \cdot 55.5 = .8 \cdot 10^{-16} \]

Because of the exceptionally low degree of dissociation; the equilibrium constant of water in the Law of mass action can be regarded to always be a certain value (55.5 mol/dm\(^3\)) furthermore, can be put together with \( K_d \):

\[ K_d = 1.8 \cdot 10^{-16} \frac{[H^+][OH^-]}{55.5} \]

\[ K_d \cdot 55.5 = K_v = [H^+][OH^-] = 1 \cdot 10^{-14} \text{ mol/dm}^3 \]

Where \( K_v \) water ion product, at 25 °C 1 \( \cdot \) 10\(^{-14} \) mol/dm\(^3\)
In a neutral solution:
\[ [H^+] = [OH^-] = 1 \times 10^{-7} \text{ mol/dm}^3 \]

In an acidic medium the concentration of \( H^+ \) ions increases, similarly in an alkaline medium
the concentration of \( OH^- \) ions is increased. Knowing the concentration of one of the ions; that
of the other one can be calculated. Since the hydrogen ion concentration is relatively easy to
measure, pH by definition is expressed with it.

\[ \text{pH} = -\lg[H^+] \] (on Sörensen’s suggestion)

in neutral solution: \([H^+] = [OH^-] = 1 \times 10^{-7} \text{ mol/dm}^3\)

Example:
\[ \text{pH} = 9.25 \quad \lg[H^+] = -9.25 = 0.75-10 \quad [H^+] = 5.62 \times 10^{-10} \text{ mol/dm}^3 \]

A pH scale and the typical intervals. (A pH can also be negative if \([H^+] < 10^{-6} = 1 \text{mol/l})

**Acids-Bases**

Acids are the molecules or ions that tend to transfer protons; bases being those capable of
withdrawing protons.

Strong acids: HCl, HNO₃, H₂SO₄, HClO₄
Weak acids H₂CO₃, CH₃COOH

Strong bases: NaOH, KOH, Ca (OH)₂
Weak base: NH₄

Dissociation of *monovalent* acids in water:
HCl + H₂O ↔ H₃O⁺ + Cl⁻

Dissociation of *multivalent* acids (e.g.: sulfurous):
H₂SO₃ ↔ HSO₃⁻+H⁺
HSO₃⁻ ↔ SO₃²⁻+H⁺

All the processes can be characterised by the equilibrium dissociation constant.

**Hydrolysis of Salts**

Interpretation of pH in aqueous salt solutions:

Sodium-acetate, CH₃COONa (weak acid – salt of a strong base)
CH₃COONa+H₂O ↔ CH₃COOH+Na⁺ + OH⁻ → alkaline

Sodium-carbonate, Na₂CO₃, soda (strong base – salt of a weak acid)
Na₂CO₃ ↔2Na + CO₃²⁻
CO₃²⁻+H₂O↔HCO₃⁻+OH⁻

→alkaline
HCO₃⁻+H₂O↔H₂CO₃+OH⁻
The proton affinity of carbonates and acetates are higher than that of water, the solutions pH is basic in this case because of the hydroxide ions set free.

Ammonium-chloride, NH₄Cl (weak base - strong acid salt)
NH₄⁺ + H₂O ↔ NH₃ + H₃O⁺ → acidic

The proton affinity of water is bigger than that of ammonia
Ammonium acetate, NH₄COOH (weak base - weak acid salt)
NH₄⁺ + CH₃COO⁻ + H₂O ↔ NH₃ + CH₃COOH + H₂O → neutral

The proton affinity of Ammonia and that of acetate is virtually identical.

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**Week 10 Video session:**

https://www.youtube.com/watch?v=aNEDU6EL8jc

https://www.youtube.com/watch?v=BBTcz60CNtM

https://www.youtube.com/watch?v=qklzb_6_Vho

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**Week 10 Question session:**


How is degree of dissociation calculated?

Derive the formulae of hydrolysis of salts.
Week 11: Electrochemistry. Redox processes, corrosion of metals
6. Electrochemistry
6.1. Redox processes, redox potentials

If the substance transfers electrons it is oxidised if takes up electrons then reduced. Just like free protons (H⁺) are not present in the aqueous solutions of acids, there are no such free electrons there either; consequently the oxidisation and reduction can only take place simultaneously together. E.g.: The reaction of Zinc with hydrochloric acid solution:

\[ \text{Zn} + 2 \text{HCl} = \text{ZnCl}_2 + \text{H}_2 \]

Oxidised reduced

Written up with ionic equation:

\[ \text{Zn} + 2\text{H}^+ + 2\text{Cl}^- = \text{Zn}^{2+} + 2\text{Cl}^- + \text{H}_2 \]

Both sides of the equation must be equal in terms of the sums of the charges of the ions.

The equation of the reaction taking place between the aqueous solution of the Copper-sulphate (blue vitriol) and the zinc metal:

\[ \text{CuSO}_4 + \text{Zn} = \text{ZnSO}_4 + \text{Cu} \]

Written up with simplified ionic equation:

\[ \text{Cu}^{2+} + \text{Zn} = \text{Zn}^{2+} + \text{Cu} \]

Under such circumstances the Zinc atoms transfer a portion of their electrons directly to the Copper ions getting in touch with them. However, processes involving electron transfer or take up can be spatially separated to some extent. That is how we arrive at the galvanic cell capable of producing electric current. The structure of the so-called Daniell cell is depicted in Figure 52. Zinc rod is immersed into Zinc-sulphate, and Copper rod is immersed into Copper-sulphate solutions of 1 mol/l concentration each.

![Figure 52. The structure of the Daniell cell [34]](image)
If there is no metallic connection, electric double layer is formed on the interface of the metal and the solution. The Zn tries to dissolve while transferring electrons (Figure 53). The leftover negative charges on the metal and the positive charges of the Zinc ions got into the solution however, attract one another. For that reason and the repulsive effect of the positive Zinc ions gathered around the metal, there can be just a very limited number of metallic ions going into the solution. An electric double layer formed between a metal and a solution may cause equilibrium potential difference that is referred to as electrode potential (ε). In case of the Copper electrode the situation is the other way around, since there the Copper ions present in the solution are trying to fall-out on the surface of the Copper. Consequently the metal is positive, the solution however, because of the excess anions, is of negative charge. On this metal the electric double layer and the electrode potential typical of the metal is formed as well.

If a metallic connection is established between Zn and Cu, moreover a diaphragm or salt bridge is put between the electrolyte solutions (the porous diaphragm blocks the mixing of the solutions however, means no obstacle for electric current or for the ions), the electrons transferred by the Zinc get to the Copper ions via the conductor. Thus, the negative edge of the battery is going to be the Zn electrode (anode) as the Cu being the positive one (cathode). The Zn plate is dissolved, while Cu falls out on the Cu plate. The current enters the solution through the anode. The ordinary denotation of the galvanic cell now obtained is:

- Zn/ZnSO₄//CuSO₄/Cu +

By convention, the potential of the positive pole of the galvanic cell is having the positive sign.

Salt bridge:

A salt bridge, in electrochemistry, is a laboratory device used to connect the oxidation and reduction half-cells of a galvanic cell (voltaic cell), a type of electrochemical cell. It maintains electrical neutrality within the internal circuit, preventing the cell rapidly running its reaction to equilibrium. If no salt bridge were present, the solution in one half cell would accumulate negative charge and the...
solution in other half cell would accumulate positive charge as the reaction proceeded, quickly preventing farther reaction, and hence production of electricity. ([https://en.wikipedia.org/wiki/Salt_bridge](https://en.wikipedia.org/wiki/Salt_bridge))

Apart from the metal electrodes, gas electrodes are known as well. **Figure 54.** shows the built-up of the Hydrogen electrode. Since under normal circumstances gases are non-conductive, the presence of an electron mediator is necessary in-between the gaseous phase and the solution. For that purpose, the Platinum is suitable, in which Hydrogen is able to be dissolved to some extent and the Hydrogen atom thus created is ionised. The potential of the Hydrogen electrode is defined by the following process:

\[ \frac{1}{2}H_2 \rightarrow H^+ + e^- \]

The Platinum immersed into hydrochloric acid solution also by itself maintains the electric connection.

**Figure 54.:** Built-up of the Hydrogen electrode [36]

**Figure 55.** Depicts a glass electrode capable of measuring the Hydrogen ion concentration (pH). The lower part of it is a thin glass membrane in which a solution of constant Hydrogen ion content can be found with a Platinum wire outlet. If the outer surface of the membrane interacts with a Hydrogen ion - containing solution that is to be measured, difference in potential is formed in function of the pH.
If there is no current flowing through the galvanic cell, the difference in potential between the poles is called electric force (E). Its measure depends on the material quality, the concentration and the temperature. Since current goes through the electrodes in opposite directions (from the electrode to the solution and the other way around), the difference is expressed as:

\[ E = \varepsilon_1 - \varepsilon_2 = \varepsilon_{\text{cathode}} - \varepsilon_{\text{anode}} \]

\( \varepsilon \) value can be expressed with the help of the Nernst equation:

\[ \varepsilon = \varepsilon_0 + \frac{RT}{zF}\ln c \]

Where
- \( \varepsilon_0 \) – material constant
- \( R \) – Universal gas constant
- \( T \) - Temperature
- \( Z \) – valency of the ions participating in the electrode process
- \( F \) - Faraday constant (Coulomb/mol)
- \( c \) - ion concentration (mol/dm\(^3\))

Converting to 10-based logarithm, at 25 °C the Nernst equation is:

\[ \varepsilon = \varepsilon_0 + (0.059/z)\log c \]

If \( c = 1 \text{ mol/dm}^3 \), \( \varepsilon = \varepsilon_0 \), therefore \( \varepsilon_0 \) is the electrode potential concerning a supposed unit ion concentration. About its absolute value; it cannot be measured therefore \( \varepsilon_0 \) is regarded to be the potential that the electrode in question shows related to the Hydrogen electrode selected for comparison. The above described method is not confusing by any means, as we always work with potential differences. If each electrode solution is of 1 mol/ dm\(^3\) and the pressure of the H\(_2\) is 1 bar, at 25 °C the so-called normal potential (standard potential) is obtained. In the
followings, the normal potentials of some well known metals are given. Please note that in many cases, the values may vary according to the source of literature. Reason being the multiple oxidisation states of metals realised. (e.g.: Fe, Sn, etc.):

Potassium (K)  
Magnitude (Mg)  
Aluminium (Al)  
Zinc (Zn)  
Iron (Fe)  
Hydrogen (H)  
Tin/Stannic (Sn)  
Copper(Cu)  
Silver/Argent (Ag)  
Mercury/Quicksilver (Hg)  
Platinum (Pt)  
Gold (Au)  

Metals having more negative normal potentials than Hydrogen dissolve in acids releasing Hydrogen while those having more positive normal potentials do not perform such abilities. Any metal can be made to be fallen out of a solution with a help of another metal having more negative normal potential. If direct current is conducted into an electrolyte solution (Figure 56.), electrolysis takes place within the system. Here the negative pole of the current source is the cathode thus the positive being the anode. The current enters the solution and the system through the positive pole. By convention, the direction of the current is opposite to the direction of the flow of the electrons. The positively charged cations head to the cathode where they take up electrons (are reduced), while the negatively charged anions make their way towards the anode where they release electrons (are oxidised).

Figure 56.: Depiction of the electrolysis [38]
6.2. Corrosion of metals

The overwhelming majority of the common metals is not in thermodynamic equilibrium with the surrounding medium. In nature, their oxidised forms (oxides, sulphides) are the stable ones, and occur in their minerals. The key step here producing metals from their ores is always the reduction:

\[ M^+ + e \rightarrow M \]

ion oxidised metal reduced state state

During corrosion, the oxidation procedure taking place eventually results in a thermodynamically stable state

\[ M \rightarrow M^+ + e \]

metal ion oxidised reduced state state

Corrosion processes

The transition from metallic state to non-metallic compounds takes place via chemical or electrochemical processes. Meanwhile, from the metallic crystal structure, metallic ion and an equivalent electron is ripped off, provided the released energy, upon reaction product formation, is of adequate quantity.

Chemical corrosion

Upon chemical corrosion the egress of the metallic ion and the electron takes place within 0.4 nm of distance. Such process is responsible for:

- the formation of the oxide layer on Aluminium (Al₂O₃) that is solid, protecting the metal from further corrosion.
- the chemical reaction of iron oxidation in the hot rolling mill. That oxide layer however, is porous.
- the blacekning of silver objects in the presence of Sulphur compounds.

Electrochemical corrosion

During an electrochemical type of corrosion happening only when electrolyte (e.g.: water) is present, the egress of the metallic ion and that of the electron is spatially separated.
Anodic sub process in case of iron:

Fe → Fe^{2+} + e

Cathodic sub process (pH dependent)

pH > 4 the Oxygen at present takes up the electron

a) \( 4e + O_2 + 4H^+ \rightarrow 2H_2O \)

b) \( 4e + O_2 + 2H_2O \rightarrow 4OH^- \)

pH < 4 the Hydrogen ion can take up the electron as well

\( 4e + 4H^+ \rightarrow 2H_2 \)

**Factors influencing metal corrosion**

a) Formation of difference in potential

At the offset of the electrochemical corrosion, difference in potential of some measure is necessary. One possibility for that is the contact of two different metals. Such corrosion procedure (contact corrosion) takes place in the presence of moisture with protective layers of metals damaged. Which metal is dissolved (oxidised) during the process is defined by the normal potentials, little known fact however, that those are dependent on the electrolytes, the temperature etc. That even implies a possible change in the order. Due to the alloying elements and pollutions in the metal; galvanic cells can also take shape. A frequent cause of corrosion is the difference in potential induced by the surrounding medium or the external effects. For instance, a galvanic cell can be created between an abraded and an intact surface of the same metal or between the heat treated and the untreated surfaces. An additional case might be the metal in contact with the heterogeneous electrolyte. The latter is also responsible for the so-called atmospheric corrosion of iron as well as the corrosion of underground pipelines.

b) pH

The Hydrogen ion concentration of the surrounding ambience influences the rate of corrosion. A typical correlation is observable between the pH and the normal potential of the metal, which is showcased by the Pourbaix diagram in case of Iron (Figure 57.) The various areas depicted stand for the different corrosion tendencies of the Iron. Clearly above 9 as a pH value, Iron is in passive state in a wide interval of potentials. The Aluminium is stable in neutral medium although acids and lies (bases) can initiate interactions.
c) Oxygen concentration
Oxygen is essential to corrosion processes. The rate of corrosion is enhanced in Oxygen rich environment.

d) Moisture content, polluted medium
The aforementioned two are capable of enhancing the rate of corrosion.

e) Increasing the temperature
Increases the rate of the process alike.

**A couple of corrosion damage**

**Contact corrosion**

Figure 58. Illustration of the electrochemical corrosion occurring as a result of the damage sustained by the Tin and Zinc protective layers on Iron. To the launch of the reaction the necessary potential difference is provided by the contact of two different metals. The electrolyte (water) necessary to the process is in abundance regarding precipitation or the moisture content of the air, the same goes for the Oxygen and the air. Upon the damage
sustained by the Tin, the Iron, having more negative normal potential (“less noble, less precious”), is oxidised. \( \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e} \), while in the other example – because of the same reasons – the Zinc goes into the solution \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e} \). The electrons transferred by the metals are taken up in both cases by Oxygen.

![Diagram of sacrificial and noble coating]

**Figure 58.** Contact corrosion in case of various protective coatings [40]

**Corrosion induced by the dissimilarity of the ambience**

**Figure 59.** illustrates the atmospheric corrosion of Iron. The dissolved Oxygen concentration is non-uniform all over the drop of water situated on the surface of the Iron: around the edges it is higher; in the middle it is lower. This very concentration difference makes the formation of a galvanic cell possible on the Iron. Wherever the Oxygen concentration is lower, anode takes shape and Iron is dissolved, while at edge regions of higher Oxygen content cathode is formed. In the cathodic process the Oxygen takes up electrons transferred and put to the edges by the Iron.

![Diagram of local cell formation]

**Figure 59.** Local cell formation on Iron surface due to a drop of water [4]
The ferrous ions ($\text{Fe}^{2+}$) with the hydroxide ions formed in the cathodic process ($\text{OH}^-$), are converted into iron hydroxide ($\text{Fe(OH)}_2$) in the drop of water, then through further oxidisation and conversion processes they form rust ($\text{FeO(OH)}\cdot\text{Fe}_2\text{O}_3$).

**Figure 60.** in the case presented the underground Iron pipe is exposed to a medium of different moisture and Oxygen content. More Oxygen can be found in a dry soil (even cracks, voids strengthen that) and less in water. As a result of the Oxygen content difference and the presence of the water, corrosion cell is developed i.e. the Iron is dissolved in an anodic way from the direction of the lower Oxygen content water.

![Diagram of electrochemical corrosion](image.png)

**Figure 60.:** Electrochemical corrosion of an Iron pipe laid in soil [41]

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**Week 11 Video session:**

[https://www.youtube.com/watch?v=lQ6FBA1HM3s](https://www.youtube.com/watch?v=lQ6FBA1HM3s)

[https://www.youtube.com/watch?v=HlGITf-rhCE](https://www.youtube.com/watch?v=HlGITf-rhCE)

[https://www.youtube.com/watch?v=T4pSuflO9fk](https://www.youtube.com/watch?v=T4pSuflO9fk)

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**Week 11 Question session:**

*Give the formulae of a couple of redox processes.*

**Essay:** Daniell and other electrochemical cells

**Essay:** Types of corrosion
Week 12: Inorganic construction binders.
Gypsum and lime
7. Binders for construction
7.1. Non-hydraulic binders
(They do not bind in water and lose their strength during long-term under water storage.)

7.1.1. Lime
The production of lime

From limestone (CaCO$_3$) or from dolomitic limestone (CaCO$_3$ \cdot MgCO$_3$), by burning.
$> \text{at } 900 \text{ C}^\circ: \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
$> \text{at } 600 \text{ C}^\circ: \text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$

The properties of the created quicklime (CaO) now received are influenced by:
- Firing temperature
  900-1000 ° C: The original crystal structure remains intact, porous, high specific surface area, "mildly" burnt quicklime is formed.
  1100-1300 ° C, the crystal structure undergoes some changes, denser, more compact, lower specific surface area,” well burnt” quicklime is produced.
- Grain Size
  Upon burning chunks of limestone of uneven grain size distribution the smaller ones over burn.
- MgCO$_3$ content
  From the over burnt Magnesium-Carbonate; Magnesium-Oxide is formed.

The slaking of lime

The slaking process is dangerous given that the Calcium-hydroxide is strongly alkaline, vitriolic and the amount of heat developed is large.

$$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{heat}$$

The mildly burnt lime is quickly (5-10 minutes), the well burnt lime and the over burnt limes are slaked slowly. The former is the so-called rich lime while the latter being the dolomitic lime. In many cases, slaking only takes place after construction, which process includes volumetric growth as well as spalling. Therefore, idle conditions are to be maintained for the sake of the lime deposition, continuously for a couple of weeks prior to the construction.

The solidification of lime

The Calcium-hydroxide takes up Carbon-dioxide from the air and is converted to Calcium-carbonate:

$$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$
The process is time consuming; the combustion can be accelerated however, by burning coke (Carbon-dioxide is formed, heat generated). Shrinkage takes place during solidification.

7.1.2. Gypsum

a) Natural plasters

Gypsum is hydrate water free in nature, that is, anhydrite (CaSO$_4$) and also occurs naturally containing water of hydration (CaSO$_4$·2H$_2$O), i.e. in gypsum form. If the gypsum is burnt at 110-180 °C then according to the following formula:

$$\text{CaSO}_4\cdot2\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot\frac{1}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2\text{O}$$

the obtained material is the hemihydrate plaster. The material at hand is also called building plaster. This very gypsum type binds and solidifies rather rapidly with water.

$$\text{CaSO}_4\cdot\frac{1}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O}$$

The so-called gypsum screed used widely in architecture is manufactured at 600-1200°C. This gypsum predominantly consists of anhydrite but basic Calcium-Sulphate of CaSO$_4$·CaO consistency can also be found in it. The gypsum screed sets slower than the building plaster but it is of higher strength. Gypsum burnt at medium temperatures possesses different properties: Between 180-300°C bondable anhydrite is formed (CaSO$_4$), while between 300-600°C over burnt anhydrite (CaSO$_4$), that due to the permanent changes in its crystal structure can only take up little to no water consequently can only perform little to no solidification.

By grinding the hemihydrate plaster, mixing it with alum, borax or with another metal salt for that matter, finally re-burning the mixture at 800°C, a high strength material, the so-called marble plaster is obtainable.

b) Synthetic gypsums

Gypsum is also generated as a by-product of various industrial processes. For instance, at desulphurisation of flue gases with limestone, REA gypsum is formed (fine texture, Calcium-sulphate-dehydrate).

**REA gypsum:**

Germany’s Federal Emission Control Law of 1983 states that power stations with fossil fuel based combustion plants must be equipped with (...) combustion gas desulphurisation plants (in German: Rauchgasentschwefelungsanlagen) hence the name REA. The implementation of this law was a great step in nationally reducing air pollution. It is a simple, wet cleaning method using natural lime and finally producing moist, particulate flue gas gypsum – REA gypsum – that can be directed straight into the economic cycle of the building material industry. Both the desulphurisation technology and the development of methods of using this REA gypsum in the building material industry are based on the results of our research (Knauf) and development work, our know-how and our close cooperation with power station operators. These methods now prevail in both western and eastern Europe: This is a fine example of European cooperation and an important contribution to the global protection of nature and
the environment. REA gypsum develops as a result of the same physical laws that govern the development of natural gypsum. The only difference being that this process takes place in fast motion within a few hours, whereas nature needed millions of years to form the layers of gypsum.


Week 12 Video session:

https://www.youtube.com/watch?v=9LDG9cnGjDo

https://www.youtube.com/watch?v=luHyJboQ5Tk

https://www.youtube.com/watch?v=9w2wAssTcYg

Week 12 Question session:

Give the formula of lime slaking

Highlight the difference between natural and synthetic plasters.

Essay: REA gypsum origins, significance and impact nowadays
Week 13: Inorganic construction binders. Cement

Portland cement, hardening, solidification, raw flour, rotary kiln, drying, preheating, calcinations, shrinkage, cooling, semi-hydrate, pseudo bonding, lime, CSH, hydraulic complement, blast furnace slag, fly ash, pig iron, tuff, CAH
7.2. Cement (hydraulic binder)
(Also sets under water (solidifies) and performs no strength loss upon long-term storage underwater.)

7.2.1. Silicate cement (Portland cement)

Basic components of pure Portland cement:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>75-80%</td>
<td>$\rightarrow$ CaO</td>
</tr>
<tr>
<td>Clay</td>
<td>20-25%</td>
<td>$\rightarrow$ Si$_2$O$_5$, Al$_2$O$_3$, Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Gypsum stone</td>
<td>5%</td>
<td>(setting regulator)</td>
</tr>
</tbody>
</table>

Raw materials of heterogeneous cements

as seen before+
hydraulic complements (fly ash, blast furnace slag, tuff) and / or limestone flour

Manufacturing process

a) Clinker production

Burning of raw flour (clay + limestone grist), in a rotary kiln:

Drying takes place with face-flowing exhaust gases coming from the opposite direction.

Preheating: around 450-550 °C, clay minerals lose their water of crystallisation, at temperatures ranging between 600-800 °C, the MgCO$_3$ becomes de-carbonated ($\rightarrow$ MgO)

Calcination: >900 °C CaCO$_3$ becomes de-carbonated ($\rightarrow$ CaO), around 1200 °C silicate producing reactions kick in.

Shrinkage: up to 1450 °C. Within the frame of exothermic process of clinker minerals are formed.

Cooling, resting: Through this, free CaO reacts with water in the air, and with Carbon-dioxide (subsequent transformation would cause swelling)

b) Cement production

The cooled down clinker is grinded up with the gypsum stone and – in case of heterogeneous cement production – grinded or added to hydraulic complements.

It is of utmost importance that the clinker is cooled adequately, because

- Hot grinding damages the crushing plants,
- Reactive semi-hydrate can be formed from gypsum-stone - , which when used in cement, hardens rather quick with water (pseudo bonding)
The oxide composition of Portland cement:

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Percentage Range</th>
<th>Other Ingredients</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>60-67%</td>
<td>free CaO</td>
</tr>
<tr>
<td>SiO₂</td>
<td>19-24%</td>
<td>other ingredients (Na₂O, K₂O, TiO₂, SO₃, etc.)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2-8%</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2-6%</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>1-5%</td>
<td></td>
</tr>
</tbody>
</table>

Types of clinkers minerals and their characterization

Silicate chemistry abbreviations: C = CaO, S = SiO₂, A = Al₂O₃, Fe₂O₃, F = H = H₂O, furthermore Cs = CaSO₄, and CH = Ca (OH)₂

The 3CaO SiO₂, alit, tricalcium-silicate (abbr.: C₃S), is the main clinker mineral having large initial strength and high bonding temperature. The amount of it in cement: 37 to 60%

• The 2 SiO₂ CaO, Belite, di-Calcium-silicate (abbr.: βC₂S), is having slow initial hardening, small bonding temperature and favourable post hardening properties. Its amount in cement by percentage is: 15-37%

• 3CaO Al₂O₃, Felite, tricalcium-aluminate (abbr.: C₃A), the fastest bonder, the most heat developer clinker mineral showcasing poor Sulphate resistance (to retard processes gypsum is added). Amount in cement: 7-15%

• Al₂O₃ Fe₂O₃ 4CaO Celite, tetracalcium-aluminate-ferrite (abbr.: C₄AF), low strength, favourable Sulphate-resistance

Typical moduli (based on the oxide composition)

Hydraulic modulus:

\[ HM = \frac{CaO\% - 0.7SO_2\%}{SiO_2\% + Al_2O_3\% + Fe_2O_3\%} \]

In case of normal Portland cement its value ranges between 1.7 and 2.3

Silicate modulus:

\[ SM = \frac{SiO_2\%}{Al_2O_3\% + Fe_2O_3\%} \]

In case of normal Portland cement its value ranges between 1.6 and 3.2

Aluminate modulus:

\[ AM = \frac{Al_2O_3\%}{Fe_2O_3\%} \]
In case of normal Portland cement its value ranges between 0.6 and 2.5 (in case of Sulphate-resistant cements it is a maximum of 0.7% and 1.0% for the mildly Sulphate-resistant cements).

**Setting and hardening of cement**

Adding water to the cement clinker minerals inside are hydrated (water is bonded in the form of Calcium-silicate hydrates and Calcium-aluminate hydrates). First gel-like, later crystalline substance (cement stone) is produced.

Processes taking place during setting, solidification:

\[
2 \text{(3CaO} \cdot \text{SiO}_2) + 6\text{H}_2\text{O} = 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{Ca(OH)}_2
\]

With short notation:

\[
2\text{C}_3\text{S} + 6\text{H} = \text{C}_3\text{S}_2\text{H}_3 + 3\text{CH}
\]

\[
2 \text{(2CaO} \cdot \text{SiO}_2) + 4\text{H}_2\text{O} = 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + \text{Ca(OH)}_2
\]

With short notation:

\[
2\text{C}_2\text{S} + 4\text{H} = \text{C}_3\text{S}_2\text{H}_3 + \text{CH}
\]

**Simplified setting, hardening process:**

*Cement (main clinker minerals) → CSH + water + lime*

CSH: Calcium-silicate hydrates, strength providing phase

lime: (Calcium-hydroxide), (pH ≈ 12.3) provides alkaline medium (in such environment the CSH phases are stable, reinforcing steel bars are passive)

*Hydraulic complements* in the heterogeneous cements consume quicklime generated upon binding, thus their mixing ratio is limited.

*Blast furnace slag*: Molten slag cooled with cold water at pig-iron production contains adequate amount of amorphous constituents bondable with exciter (lime and SO\(_3\)). Because of it SO\(_3\) content it is reactive on its own as well. Maximum mixing ratio: 80%.

*Fly ash*: ash of coal dust burning power plants. It binds with Calcium-hydroxide. Maximum amount is 35%.

*Tuff*: natural cinder. It binds with Calcium-hydroxide. Maximum amount is 20%.

**Bond regulatory role of gypsum stone**

In the absence of plaster rock 3CaO • Al\(_2\)O\(_3\) (C\(_3\)A) and from the reaction of water Calcium-aluminate-hydrates are formed with fast reaction:
\[ 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{Ca} (\text{OH})_2 + 12\text{H}_2\text{O} = 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O} \]

With short notation:
\[ \text{C}3\text{A} + \text{CH} + 12\text{H} = \text{C}4\text{AH}13 \]

\[ 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 6\text{H}_2\text{O} = 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} \]

Short notation:
\[ \text{C}3\text{A} + 6\text{H} = \text{C}3\text{AH}_6 \]

Simplifying the process described above:
\[ \text{C}3\text{A} + \text{water} \rightarrow \text{CAH} \]

CAH = Calcium-aluminate-hydrates, hardening rather fast while developing considerable amount of heat. Due to the above process, the cement would set fast, which in many cases, would make it impossible to be used up. In the presence of gypsum stone, not the aforementioned accelerated process takes place but ettringite (trisulphate) is formed that is a non-solidifying phase.

\[ 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 26\text{H}_2\text{O} = 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \]

Short notation:
\[ \text{C}3\text{A} + 3\text{Cs} + 32\text{H} \rightarrow \text{C}3\text{A} \cdot 3\text{Cs} \cdot \text{H}_{32} \]

This process is quick as well and involves swelling but there is still room in the pulp for large hydrate-water-content ettringite to form.

The ettringite later transforms into a monosulfate (\( \text{C}3\text{A} \cdot \text{Cs} \cdot \text{H}_{12} \)).

In Figure 61. The change of the amount of the reaction products formed during cement setting can be contemplated in time.

![Figure 61](image-url)
**Week 13 Video session:**

https://www.youtube.com/watch?v=dyxL_BvkhJg

https://www.youtube.com/watch?v=hBqhGHfzQFQ

https://www.youtube.com/watch?v=wfli_rHnhZM

**Week 13 Question session:**

*What do these abbreviations stand for?:* CSH, CAH

*Define the following terms:* semi-hydrate, hydraulic complement, pseudo bonding, pig-iron.

*Characterise the following complements:* blast furnace slag, fly ash, and tuff.
Week 14: Inorganic construction binders.
Factors influencing the binding of cement.
Cement corrosion
Factors influencing the rate of bonding and setting of cement

Degree of grain fineness

Smaller the particle greater the surface area and faster the reaction with water is. The inside of the smaller particles (<20 μm) also hydrates, while in case of the larger particles it is only the surface layer that does so (The hydrate layer prevents the penetration of further water). The final strength (Ultimate Limit State) of finer cements is also greater.

Temperature

An increment in temperature usually increases the chemical reactions, thus the rate of hydration of cement.

According to (Nurse-)Saul equation (applied to concretes)

\[ k = \Sigma \Delta t_i (T_i + 10) \]

where

- \( k \) is the degree of maturity (→ strength)
- \( T_i \) is the average temperature at \( \Delta t_i \) in °C

The solidification ceases at -10 °C.

Admixtures/additive

Accelerators speed up the hydration as a catalyst, but short-fibre products are formed, therefore the final strength is smaller (similarly to the so-called steam aging solidification at higher temperature). Retarders slow down the hydration, but will increase the proportion of long-fibre products increases as well as the final strength.

Transformation processes in the hardened cement (cement stone)

Carbonation

Carbonation process as a result of the \( \text{CO}_2 \) content of the air:

\[ \text{Ca (OH)}_2 \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]

During the process, the pH gradually decreases; as well as the passivation of reinforcing steel.

Metathesis corrosion

Mainly as a result of \( \text{Mg}^{2+} \) - and \( \text{NH}_4^+ \)- ion-containing water metathesis reaction takes place:

\[ \text{MgCl}_2 + \text{Ca (OH)}_2 + \text{CaCl}_2 = \text{Mg (OH)}_2 \]
In the process the amount of Calcium-hydroxide phase decreases, in place of it highly soluble Calcium-chloride and washed out Magnesium-hydroxide is formed. The ammonium salts (because of their better solubility) are even more dangerous.

**Effect of acids**

The strong and weak, furthermore the organic and inorganic acids (hydrochloric acid, sulfuric acid, nitric acid, carbonic acid, acetic acid, lactic acid, formic acid) in addition to Ca (OH)$_2$ phase, dissolve even the Calcium-carbonate formed during the carbonation.

Reaction due to Hydrochloric acid:

\[
\text{Ca} (\text{OH})_2 + 2\text{HCl} = \text{CaCl}_2 + 2\text{H}_2\text{O} \\
\text{CaCO}_3 + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{CO}_3
\]

Reaction due to sulfuric acid:

\[
\text{Ca} (\text{OH})_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{H}_2\text{O} \\
\text{Furthermore: } \text{CaSO}_4 + 2\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}
\]

Thus, ultimately gypsum is formed, which can cause corrosion associated with volume increment. The process results in cement stone pH value decrement. Reaction with carbonic acid:

\[
\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightarrow \text{Ca} (\text{HCO}_3)^2 \rightarrow \text{CaCO}_3 \text{ (powder)} \text{ and } \text{H}_2\text{CO}_3
\]

whereby water-soluble Calcium-hydrogen-carbonate is formed that with carbonic acid loss, forms Calcium-carbonate ("karstification" process)

**Chemical reactions causing volumetric growth**

As a result of industrial and ground waters containing Sulfate ions ettringite can be formed even with the bonded C$_3$A phase of cement, resulting in a substantial increase in volume and cracks:

\[
\text{Na}_2\text{SO}_4 + \text{Ca} (\text{OH})_2 = 2\text{NaOH} + \text{CaSO}_4 \\
\text{CaSO}_4 + 2\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \\
\text{C}_3\text{A} + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 30\text{H}_2\text{O} = \text{C}_3\text{A} \cdot 3\text{CS} \cdot \text{H}_3\text{2}
\]
7.2.2. Aluminate cement (aluminous)

Base material: limestone and Aluminium containing rock (e.g. bauxite) Mainly fast setting Calcium-aluminates are produced (e.g.: C₃A) in the burning process. The aluminate cement solidifies rapidly and exothermically while Calcium-aluminate hydrates take form. A significant portion of the hydrates are unstable and are transformed into Aluminium-hydroxide and Calcium-carbonate with time while the strength is greatly reduced. Today it is mainly used as cementing material of fire-resistant concretes.

**Week 14 Video session:**

https://www.youtube.com/watch?v=49Tw245g6aE

https://www.youtube.com/watch?v=-u5mgRLVGFA

https://www.youtube.com/watch?v=2SKSgqtKzlM

**Week 14 Question session:**

*What is aluminate cement? What is it used for nowadays?*

*Give the chemical formula of cement carbonation.*

*List the chemical reactions associated with cement hardening that imply volumetric growth.*
Stereograms

Cover: 

Week 1: 

Week 2: 

Week 3: 

Week 4: 

Week 5: 

Week 6: 

Week 7:
Week 8: 

Week 9: 

Week 10: 

Week 11: 

Week 12: 

Week 13: 

Week 14: 

Create your own stereogram at: 
http://www.flash-gear.com/stereo/
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