Basics in Chemistry
Materials, Mixtures, Elements, Atoms, Compounds

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Chemistry – Definition
Chemistry is the Science of material properties and their interactions

Tasks for a Chemist in Construction Industry
• Product Development
• Development of New Technologies
• Analysis of Damages
• Quality Control
Material properties

1. Odour
2. Taste
3. ....
4. Thermal conductivity
5. Electrical conductivity
6. Density
7. Solubility
8. ....

Electrical Conductivity

Electrical conductivity is decisive for the rate of corrosion of the reinforcement.

\[ \sigma = \frac{1}{\rho} \left( \frac{1}{\Omega \cdot \text{m}} \right) \]

Electrical conductivity is the reciprocal value of the electrical resistance.

Solubility

Solubility = \( \frac{\text{Mass of material}}{\text{Volume Solvent}} \)

\[ L = \frac{m}{V} \left( \frac{\text{kg}}{\text{m}^3} \right) \]
Solubility – in practice

Example: Ettringite formation
In hardened cement paste insoluble ettringite is formed in the presence of sulphate which precipitates in the pores.

Example: Alkaline depot
During the cement hydration calcium hydroxide is formed. Only a small amount of Ca(OH)₂ is dissolved in the pore solution.

Materials

Definition: Materials
It’s a kind of substance and a uniform shape of matter.

Example: Iron

Material – in Practice

Example: Styropor (polystyrene)
Styropor is a polymer formed by polymerisation of monomers
Element

Definition: Element
An element is a material, which can not be separated by chemical techniques.

Mercury (Hg)

The Periodicity of Elements

DÖBEREINER - TRIPPLES (1816)
Formulation of Tripples (similar properties), dependence to atom mass

NEWLAND – OKTAVES (1865)
Arrangement of elements which are similar in chemical behaviour and by increasing atom mass.

MEYER und MENDELJEWS - „PSE“ (1868 alternatively 1869)
Arrangement of elements by atom mass and density (Meyer) and similar chemical behaviour (Mendeljew), forecast of later found elements.

The Periodic Table of Elements

Alkaline metals: melting point Li=168 °C → Cs=29°C
Noble gas: very inactive regarding reactivity
Metals: Ti, V, Cr, semi-conductors: Si, Ge, As, ...
Elements

Today 112 elements are known, 91 elements can be found in nature.

Each element is named and characterised by a symbol:
- Ca = Calcium
- Si = Silicon
- O = Oxygen
- C = Carbon

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Structure of Matter – Element

Definition: **Element**
A chemical element is build-up by atoms with the same chemical properties.

Silicon
Semi-conductors: 1 Atom per 10° Atoms

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Structure of Matter – Atom

Definition: **Atom**
An atom is the smallest part of an element having all chemical properties of the element.
Structure of Atoms

An atom is built-up by a positive core and a ball-shaped electron sheath. The diameter of the atomic core is $1 \times 10^{-15}$ m (Femtometer). The diameter of an atom is approx. $100-400 \times 10^{-15}$ m (Picometer).

The structure of an Atomic Core

The atomic core is built-up by positive charged protons and non-charged neutrons. The mass of the atom (99.8%) is located in the atomic core. The atomic core is surrounded by negative charged electrons.

The Periodic Table of Elements

Alkaline metals: Melting point Li=168 °C → Cs=29°C

Noble gas: Very inactive regarding reactivity

Metals: Ti, V, Cr, semi-conductors: Si, Ge, As, ...
The Structure of the Atomic Core

- The atomic core of elements differ in their number of protons. The amount of protons is called atomic number which defines the position of the element in the periodic table of elements.
- The amount of protons is also the amount of electrons.
- The amount of neutrons can vary in elements. Elements with different amount of neutrons are called isotopes.

Chemical Compound

Definition: Compound
A compound is made of different elements which were bond together. These Compounds can be decomposed in their elements by chemical techniques.

Chemical Compounds in practice

Example: Polymer tube
Due to a chemical reaction, the so called polymerisation, monomers build up polymers.
Chemical Compound

Ion bond  Molecular bond  Metal bond

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Reaction of Chlorine with Sodium

Sodium reacts with chlorine gas under heat release. Thereby a crystalline compound called sodium chloride is formed.

\[
\text{Sodium} + \text{Chlorine} \rightarrow \text{Sodium chloride}
\]

\[
\text{Na} + \text{Cl} \rightarrow \text{NaCl}
\]

Formation of Sodium Chloride

\[
\text{Na} + \text{Cl} \rightarrow \text{Na}^+ + \text{Cl}^-
\]

As a result of the emission of electrons, positive sodium ions are formed (Cation) and as a result of the uptake of electrons, negative chloride ions are formed (Anion).
Cation or Anion?

The “PTE” shows if an element is an anion or cation in an ionic compound. Some elements (Fe, Cr, Cu...) can form more than one ion.

Crystal structure and materials properties

Metal bond

Most of all elements are metals. More than 50% of the main group elements of the PSE and all transition elements are metals!

Properties of Metals
• Thermal and electrical conductivity
• Ductility
• Metallic luster
Electron Gas-Model

**Electrical conductivity:** Transport of electrons by the action of an electric current.

**Heat transfer:** Heat is transformed to kinetic energy.

**Ductility:**
The cation layers are moved by mechanical stress.

Molecular Bond

Most of all chemical compounds are characterised by material properties which are quite different to the properties of ionic or metallic compounds.

**Material properties**
- Gas, liquid or solid
- High vapour pressure
- Ductile deformable

The Covalent Bonding

The covalent bond is formed by an electron pair, which is participated by two atoms (Lewis, 1916)

According to LEWIS an electron pair is located between the atomic core and attracts the atomic core which leads to the bond of the atoms.
The Electric Dipole

An electric dipole is characterised by a positive charge which is located next to a negative charge with the same value.

The Dipole Character of a Molecule

The polarity of bonds increases with the rising difference in the electronegativity of the elements.

Hydrogen-Bond

Experimental Results:
H₂O boils at 100 °C, H₂S boils at –60 °C. The reason for that is the formation of hydrogen-bonds.

Hydrogen-bonds are formed by hydrogen atoms located between two atoms with high electronegativity.
Transport of Aggressive Chemicals by Capillary Absorption

Liquids
Three forms of water are important in construction:
- Fluid
- Vapour
- Ice

Impacts of Water in Construction
Water may damage material in all this physical conditions:
- Fluid
- Ice
- Vapour
Hydrogen Bond

In the strong hydrogen bonds the relevant characteristics for construction are founded:
- Water vapour \( \rightarrow \) High boiling point
- Water \( \rightarrow \) Dissolving power for salts
- Ice \( \rightarrow \) Volume Increase while freezing

Chemistry of water – Anomaly of water

- Melting point curve has a negative gradient („Vats“)
- Ice (0.916 g/cm\(^3\)) has a lower density than water (0.999 g/cm\(^3\))
- The highest density of water is at 4 °C, not at 0 °C
- Volume of ice is 9-10% in excess of water

\[ \text{Freezing of watercourses} \]

Properties of fluids – Surface tension

- Fluids tend to minimize their surface.
- This State is reached by a Sphere (largest Volume with lowest Surface)
- Gravitation is the cause of water drops being not spherically
Chemistry of water – Surface Tension

- Fluids aspire to minimum surfaces (sphere)
- Inside the fluid act cohesion forces in all directions
- At the surface there is a force directed inside

\[ \text{Surface Tension} \sigma = \frac{\Delta E}{A} \text{ in N/m} \]

Resultierende Kraft \( F \)

\[ M_1 \rightarrow M_2 \]

Wetting of Surfaces

Wetting of surfaces of SOLIDS caused by FLUIDS depends on the INTENSITY of the cohesion forces (ion-ion- or ion-Dipole-Interaction)

The degree of wet-ability of a surface is the contact- or wetting-Angle
Capillary Absorption

Stands a capillary in a wetting fluid a hunched down fluid surface is formed. From the Laplace-Equation a negative pressure $p$ above the surface is received.

$$p_{\text{Laplace}} = p_{\text{Atmosphäre}} - \frac{2\sigma}{r}$$

Capillary-internal-pressure $p_{\text{Laplace}}$

The capillary negative pressure $p_{\text{Laplace}}$ the weight force $p_{\text{Weight}}$ is opposed. The climb-altitude of the fluid results from their effort to build an equilibrium.

Capillary negative pressure $p_{\text{Laplace}}$

$$p_{\text{Laplace}} = p_{\text{Atmosphäre}} - \frac{2\sigma}{r}$$

Weight-Force $p_{\text{Weight}}$

$$p_{\text{Weight}} = \rho \cdot \pi \cdot r^2 \cdot h \cdot g$$

Adhesion forces between Water and surface of the capillary is leading to ascension of the fluid

Hydrophillic = water-liking, Hydrophobic = water-repellent

Calculation of Altitude $h$:

$$h = \frac{2\sigma}{\rho \cdot g \cdot r} \text{ in m}$$

Impact:
Climbing moisture in masonry
Important Reactions

- Acid-base-reaction
- Precipitation-reaction
- Reduction-oxidation-reaction

Acid-Base-Reactions – Definition of Arrhenius

Arrhenius defines acids containing hydrogen atoms and emitting them as H⁺-Ions. Bases are defined to be able to release in aqueous solution OH⁻-Ions.

- Example:
  - CO₂ in H₂O ➔ H₂CO₃ ➔ Acid
  - Ca(OH)₂ in H₂O ➔ Base

Acid-Base-Reactions - Definitions

There are numerous definitions for acids and bases.

- Arrhenius ➔ 1887 „Chemische Theorie der Elektrolyte“, (Chemical Theory of Electrolytes)
- Brönsted ➔ 1923 Brönsted independent of Th. Lowry
- Lewis ➔ 1938 Base has a free pair of electrons, acid is able to accept a free pair of electrons

Cu²⁺ + 4 NH₃ ➔ [Cu(NH₃)₄]²⁺
Important Arrhenius-Acids and -Bases

Hydrochloric acid (HCl) and nitric acid (HNO₃) are organic acids.
Acetic acid (CH₃COOH) is an organic acid.

Important acids for construction:
H₂CO₃, HNO₃ and H₂SO₄

CH₄ (Methane) is no Acid

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Acid-Base-Reactions - Neutralisation

Neutralisation is a reaction between acid and base under formation of salt and water
HCl + NaOH → NaCl + H₂O

Bases are defined to be able to release OH⁻-Ions.

A neutralisation-reaction is often associated with a Precipitation Reaction.

Reactions between cement based materials and acid

Reaction between acid (HNO₃) and base (cement stone and calcium hydroxide) under formation of salts and water.
Acid-base-reactions according to Arrhenius

ACID: \[ \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \]
BASE: \[ \text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \]
\[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- (?) \]

BRÖNSTED-Definition for acids and bases

Acids and Bases according to BRÖNSTED
1923 Brönsted and Lowry suggested the following Definitions:
Acids are PROTON-DONOR ("Contributor")
Bases are PROTON-ACCEPTOR

Typical Representatives of BRÖNSTED-Acids and -Bases

ACID: \[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- (\text{Dissociation}) \]
\[ \text{H}_2\text{O} \text{ is a Proton-Acceptor} \rightarrow \text{H}_3\text{O}^+ (\text{BASE}) \]
\[ \text{HCl is a Proton-Donor} \rightarrow \text{Cl}^- (\text{ACID}) \]
BASE: \[ \text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \]
\[ \text{OH}^- + \text{H}_3\text{O}^+ \rightarrow 2\text{H}_2\text{O} "\text{Proton-Acceptor}" \]
\[ \text{CaO:} \rightarrow \text{O}^2^- + \text{H}_2\text{O} \rightarrow 2\text{OH}^- "\text{Proton-Acceptor}" \]
\[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- "\text{Proton-Acceptor}" \]
The Ionic-Product of Water

\[ \text{H}_2\text{O} + \text{H}_2\text{O} \Leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \]

\( \text{H}_2\text{O} \) is simultaneously Brønsted-acid and - Base

The equilibrium-reaction is called AUTOPROTOCOLYSE:

\[ k = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \]

1 Litre water is approximately equivalent 55 mol/l and is scarcely changed by autoprotolysis

\[ \left[\text{H}_2\text{O}\right] = \left[\text{H}_3\text{O}^+\right]\left[\text{OH}^-\right] \]

\[ k_w = \left[H_3O^+\right][OH^-] \quad K_w = \text{ionic-product of water} \]

The Ionic-product of water is independent from the Concentration of the several Ions

\[ [\text{H}_3\text{O}^+] >> \quad [\text{OH}^-] << \]

\[ [\text{H}_2\text{O}] << \quad [\text{OH}^-] >> \]

The H\text{3O}^+-Concentrations diversify over a large spectrum:

\[ [\text{H}_3\text{O}^+] \ldots 10^{-2} \ldots 10^{-12} \]

Definition of the pH-Value:

\[ \text{pH} = -\log [\text{H}_3\text{O}^+] \]

Sörensen defined the pH-Scale (Brewing)
Sörensen defined the pH-Scale (Brewing)

Measurement of pH-Value may take place by several Methods:
- Potentiometric Measuring Methods
- Fluid Indicators

Phenolphthalein

Fluid Indicators are organic compounds, whose colour in Solution are pH-Value dependent.

For Example Phenolphthalein, Bromthymolblau or Methylorange

7.0  pH-Wert  9.5

Phenolphthalein
**Typical Fluid Indicators**

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Color of Sauren Form</th>
<th>pH-Range of Basic Colored Form</th>
<th>pKb</th>
<th>Color of Basic Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thymolphthalein</td>
<td>rot</td>
<td>1.4 - 3.0</td>
<td>1.7</td>
<td>gelb</td>
</tr>
<tr>
<td>Metilorange</td>
<td>rot</td>
<td>3.2 - 4.4</td>
<td>3.4</td>
<td>gelb</td>
</tr>
<tr>
<td>Resorcinolblue</td>
<td>gelb</td>
<td>3.8 - 4.6</td>
<td>3.9</td>
<td>blau</td>
</tr>
<tr>
<td>Bromkresolrot</td>
<td>gelb</td>
<td>3.8 - 5.4</td>
<td>4.7</td>
<td>blau</td>
</tr>
<tr>
<td>Methylenblau</td>
<td>rot</td>
<td>4.8 - 6.0</td>
<td>5.6</td>
<td>gelb</td>
</tr>
<tr>
<td>Bromthymolblue</td>
<td>gelb</td>
<td>6.0 - 7.6</td>
<td>7.1</td>
<td>blau</td>
</tr>
<tr>
<td>Lackmus</td>
<td>rot</td>
<td>5.0 - 8.0</td>
<td>6.5</td>
<td>blau</td>
</tr>
<tr>
<td>Phenolrot</td>
<td>gelb</td>
<td>6.6 - 8.0</td>
<td>7.9</td>
<td>rot</td>
</tr>
<tr>
<td>Thymolblue</td>
<td>gelb</td>
<td>8.0 - 9.6</td>
<td>8.9</td>
<td>blau</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>farblos</td>
<td>8.2 - 10.0</td>
<td>9.4</td>
<td>pink</td>
</tr>
<tr>
<td>Allantoinblau R</td>
<td>gelb</td>
<td>10.1 - 12.0</td>
<td>11.1</td>
<td>rot</td>
</tr>
<tr>
<td>Allantoin</td>
<td>rot</td>
<td>11.0 - 12.4</td>
<td>11.7</td>
<td>violett</td>
</tr>
</tbody>
</table>

**Analysis of concrete-corrosive Water**

DIN EN 206-1 allows analysis of Concrete-corrosive Water at Construction site.

**Carbonation of reinforced Concrete**

A short historic Abstract

- 1879 Cement-Coating anticipates Rust
- 1908 Perception, that alkaline environment anticipates Corrosion
- 1916 „Corrosion for safety reasons of highest interest“
- 1919 1.5 cm Concrete-Coating should be enough to prevent Reinforcement Corrosion
Carbonation of reinforced concrete

The reaction of the CSH-phases with CO₂ is called CARBONATION.

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

Reasons for damages by carbonation

• Low cement content
• Minor dimension of cover concrete
• CO₂-content of the air
• Additional pollutants (NO, NO₂, NO₃)
• Insufficient manufacture of the concrete

Reaction steps of the carbonation

1. Diffusion of CO₂ into the cement rock
2. Solution of CO₂ in the pore solution
   \[
   \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow 2\text{H}^+ + \text{CO}_3^{2-}
   \]
3. Reaction of Ca(OH)₂ with H₂CO₃
   \[
   \text{Ca(OH)₂} + \text{H}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2 \text{H}_2\text{O}
   \]
4. Decomposition of cement rock
   \[
   \text{C}_x\text{SH}_y + x\text{CO}_2 \rightarrow x\text{CaCO}_3 + \text{SiO}_2 + y\text{H}_2\text{O}
   \]

Carbonation is a coupled process: Transport & chemical reaction

Solubility

During a dissolution process, there is a competition regarding the formation of bonding between
- the bonding between the solid phase molecules.
- the solvent and the molecules of the solid phase (hydrogen bonding)
- the solvent molecules (hydrogen bonding)
Saturation and Solubility
In a saturated solution a dynamic equilibrium exists between dissolved matter and a solid phase. The **Solubility** is the concentration of a saturated solution.

**Verification:**
- Ag↓ $^{127}$I and $^{131}$I
- Detection of radioactivity

Consequences of Carbonation
The CARBONATION has positive and negative effects on reinforced concrete.

**POSITIVE:**
- Increase of density of the structure of the concrete ($\Delta V=11\%$)

**NEGATIVE:**
- Disintegration of the passivation layer (approx. 50 nm) consisting of iron oxides – and hydroxides on the steel surface
- Steel corrosion

Corrosion of the reinforcement
Conditions for the steel corrosion
- Presence of electrolytes
- „Break down“ of the passivation layer
- Sufficient amount of oxygen
- Formation of von local spots of corrosion
Mechanisms of the corrosion of the reinforcement

The corrosion of the reinforcement is an electrochemical process.

Electrochemical reaction steps:
- Anode: \(2 \text{Fe} \rightarrow 2 \text{Fe}^{2+} + 4 \text{e}^-\)
- Cathode: \(\text{O}_2 + 2 \text{H}_2\text{O} + 4\text{e}^- \rightarrow 4 \text{OH}^-\)
- Reaction: \(2 \text{Fe} + \text{O}_2 + \text{H}_2\text{O} \rightarrow 2 \text{Fe(OH)}_2\)
- Further reaction: \(4 \text{Fe(OH)}_2 + \text{O}_2 \rightarrow 4 \text{FeOOH} + 2 \text{H}_2\text{O}\)

Corrosion of the reinforcement – important factors

The following factors influence the corrosion of the reinforcement:
- Amount of oxygen (quality of the concrete, humidity)
- Electrical resistance (humidity, salts)
- ...
Calculation of carbonation depth

Carbonation is a diffusion controlled process:

1. Fick’s law

\[
\frac{dm}{dt} = D \cdot F \cdot \frac{dc}{dy}
\]

\[
dm = m_0 \cdot F \cdot dy
\]

**Symbols:**
- \( y \) = Thickness of carbonated layer [m]
- \( m_0 \) = Absorbed CO\(_2\) mass per volume unit of concrete [kg]
- \( F \) = Area of carbonating concrete [m\(^2\)]
- \( c \) = CO\(_2\) concentration in the air and in the pore structure [kg/m\(^3\)]
- \( D \) = Diffusion coefficient [m\(^2\)/s]
- \( t \) = Time of admission [a]
- \( m \) = CO\(_2\) mass transported through the concrete surface [kg]

Mass balance

\[
\frac{dm}{dt} = \sqrt{\frac{2 \cdot D \cdot c_0}{m_0}} \cdot \sqrt{t}
\]

\[
y = k \cdot \sqrt{t}
\]

Where:
- \( k \) = Carbonation coefficient in mm/a\(^{0.5}\)

Factors affecting the depth of carbonation

- Concentration of CO\(_2\)
- Humidity
- Concrete quality (W/C-ratio)
- Type of cement
- Aftercare
- Aggregates, additives, admixtures
- Temperature