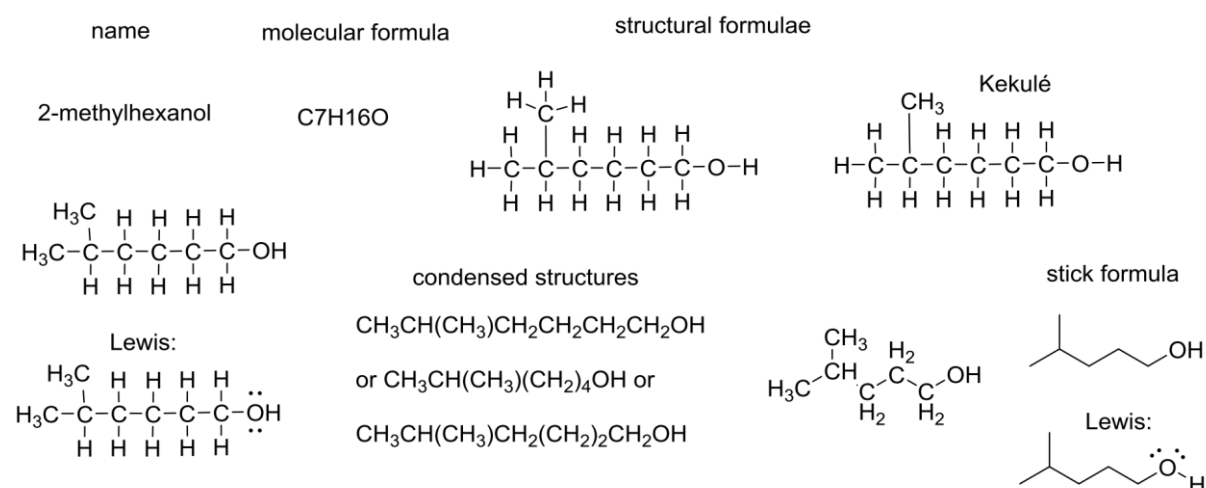


Summary Material and Molecules (based on lecture slides)

P. Deuss

Sustainability → The ability of not being harmful to the environment, society and economy

Different methods to represent molecules:



Crude oil → A very large mixture of mostly hydrocarbons

Hydrocarbon → Molecule existing only of C and H atoms

Saturated → Only single bonds in a molecule (also applicable at (un)saturated fats)

Alkane is a molecule is a hydrocarbon and saturated. All C-atoms are sp³-hybridized

Combustion (oxidation) → Measure of fuel performance. Higher for branched alkanes (isomers).

$$\text{Atom efficiency} = \frac{\text{Molecular mass desired products}}{\text{Sum of molecular mass of all reactants}} * 100\%$$

$$\text{E-factor} = \frac{\text{Amount of waste (kg)}}{\text{Amount of product (kg)}} \quad (\text{waste} \rightarrow \text{undesired product})$$

Three reaction types:

1. Coupling (addition)
 - a. $A + B \rightarrow C$
2. Breaking (elimination)
 - a. $C \rightarrow A + B$
3. Metathesis (substitution)
 - a. $A + B \rightarrow C + D$

Catalysis → Increase the rate of a chemical reaction by adding a **catalyst**. Catalyst is not consumed.

Overview of naming available at Nestor (take a look at the last few slides of Lecture 1)

Alkenes (olefins) → Unsaturated hydrocarbons, with at least one double bond. Sp²-hybridization occurs.

Polymerization → Double bond in (unsaturated) alkenes “open up” to form (saturated) alkanes.

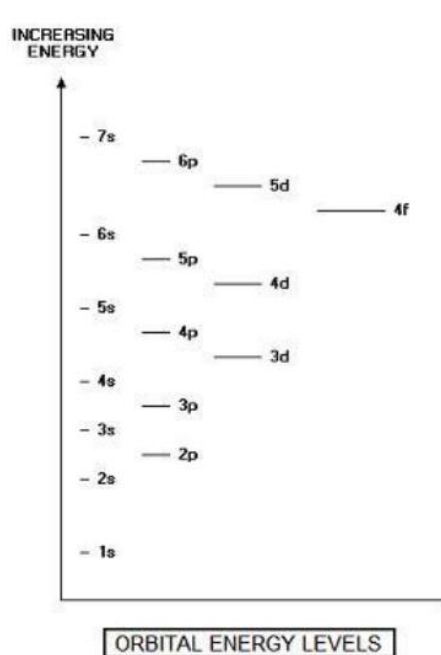
Heisenberg Uncertainty Principle → it is not possible to determine both the position and the momentum (speed) of an electron ($\sigma_x \sigma_y \geq \frac{h}{2}$)

De Broglie wave/particle duality → A wavelength can be associated to a moving particle ($\lambda = \frac{h}{mv}$)

Schrödinger equation → wave function ψ describes the energy of an electron and the probability of finding the electron in a region around the nucleus (ψ^2).

Atoms have electron “clouds”, which contain electron shells. Each shell can contain a maximum amount of electron. If a shell is filled, the next shell will be filled and so on. The valence shell is the outermost shell of an atom.

Filling atomic orbitals



Each:

s orbitals
1x2 = **2 electrons**

p orbitals
3x2 = **6 electrons**

d orbitals
5x2 = **10 electrons**

f orbitals
7x2 = **14 electrons**

Octet Rule → rule of thumb, which says that atoms tend to have 8 (octet) electrons in its valence shell. It could be said that most atoms want to be as a noble gas. The octet-rule is useful for drawing the Lewis-structure of a molecule, in which (valent) electrons are drawn at all atoms.

Covalent bond → electrons are shared between two atoms, not transferred. A pair of shared electrons constitutes a single covalent bond.

Connecting atoms

- Write each atom surrounded by its valence electrons

- Connect atoms using electron pairs, trying to reach the full octet for all of them (NB: H can only have 2 electrons = 1 bond) (octet rule works best for second row elements with only s and p orbitals)
- Use multiple bonds when necessary to reach the octet and minimize single electrons (less stable)

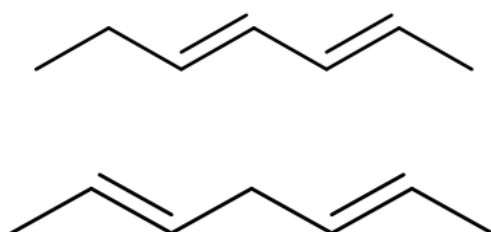
Lewis structures:

- Find the total number of valence electrons supplied by all of the atoms in the structure
- Write down the skeletal arrangement of the atoms and connect them with a single covalent bond
- Distribute pairs of electrons around each atom to give each atom eight electrons around it
- If there are not enough electrons to give these atoms eight electrons, change single bonds between atoms to double or triple bonds by shifting non-bonded pairs of electrons as needed

Resonance hybrids → Electrons are delocalized in a molecule. Think about the moving double bonds in a benzene.

Over a double bond could not be freely rotated, over single bonds it can. This is due to its hybridization. Trans-/cis molecules.

An alkene is conjugated if double bonds and single bonds occur alternately. Upper molecule is conjugated, and the bottom molecule is not conjugated.



A molecule must require 4 criteria in order to be aromatic:

1. The molecule must be cyclic
2. All atoms must have a p orbital (so sp^2 or sp^3)
3. The molecule must be planar
4. $4n + 2$ pi-electrons (odd electron pairs only!) (Hückel Rule)

Isomerism → certain chemical compounds have the same elemental composition, but different structures, chemical and physical properties.

Structural isomers → Same molecular formula, different connectivity, different functional groups, different properties.

Conformational isomerism → a molecule is an isomer due to a rotation in a single bond.

Geometric isomerism → trans-/cis molecules. Cis if all substituents are on the same side of the pi-bond (double bond). Trans if all substituents are on different sides of the pi-bonds (double bonds).

Trans-/cis molecules are more stable with more substituents. The closer the substituents to each other, the stronger (cis is stronger than trans).

Stereoisomerism → a form of isomerism in which molecules have the same molecular formula and sequence of bonded atoms but differ in their special orientation.

Chiral atom → an atom is nonsuperimposable on its mirror image. An atom with four different substituents.

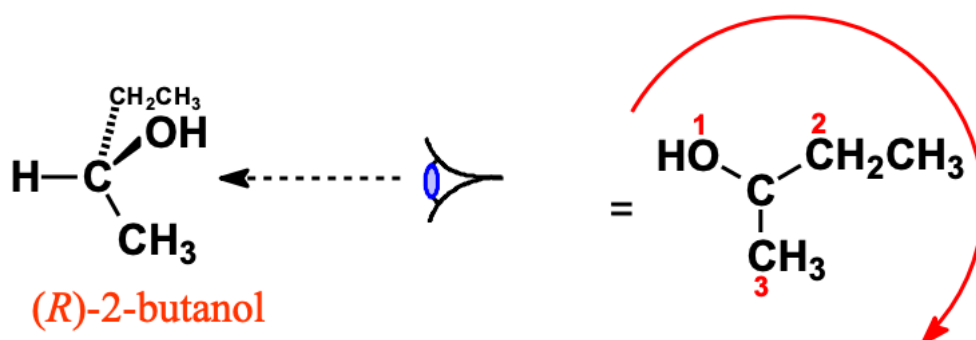
Achiral atom → Superimposable on its mirror image. The molecule could be mirrored and remain the same in space. An atom with 2 or more of the same substituents.

Enantiomer → a chiral compound (molecule with a chiral atom) and its mirror image. Same physical properties but could be distinguished by the way the polarization is rotated. Difference between clockwise (dextrorotatory, +) and counterclockwise (levorotatory, -)

Epimers → a form of stereo isomerism in which two isomers differ at only one atom (often carbon). The rest of the molecule is exactly the same.

Absolute configuration:

- Look down the bond from the chiral carbon to the smallest group.
- Assign properties to the remaining groups based on atomic numbers.
- Clockwise (highest to lowest priority) = R, counterclockwise = S



Erythro diastereomer if the substituents are eclipsed. Threo diastereomer if not eclipsed.

Meso-compound → a molecule with an internal mirror image. It could be shown as a symmetric axis, in which the one side of the axis is the mirror image of the other side.

Within the branched molecules, increased symmetry leads to a higher melting point and a lower melting point. Double bonds lead to a higher boiling point.

Polarity → The tendency of an atom to attract a bonding pair of electrons. Happens if atoms differ in electronegativity. The atom with the highest electronegativity attracts the one with the lower electronegativity.

Electronegativity → Tendency of atoms to attract electrons. Remember: an atom wants to have the same electron configuration as the noble gases.

Van der Waals- force → The attracting force between organic molecules.

The more polarized a molecule is, the stronger dipole moment it has, the more soluble in water. Solubility occurs if interaction is favorable enough to compensate for loss in intermolecular interactions of the solvent and intermolecular interactions of the solute

Amides (amino acid) → A molecule, existing of a part with an acid and a part with an amine.

Acid → A substance able to accept a lone pair of electrons from a base

Base → A substance able to donate a lone pair of electrons to an acid

pH < 7 = acidic solution, pH = 7 = neutral solution, pH > 7 = basic solution

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

$$\text{pOH} = -\log [\text{OH}^-] \text{ and } \text{pOH} = 14 - \text{pH}$$

The strength of an acid is represented by its ionization constant, K_a :

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}, \text{ p}K_a = -\log [K_a] \text{ and (strength of base) } K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]}, \text{ p}K_b = -\log [K_b]$$

If the pH of the solution is lower than the pKa, the solution is protonated (addition of a H^+ atom). If the pH is higher than the pKa, the solution is deprotonated (releases a H^+ atom).

An acid is stronger if its conjugated base is weaker (lower energy). A base is stronger if its conjugated acid is weaker (lower energy).

Stability of the conjugated base depends on:

1. Electronegativity – a higher electronegativity means a stronger and more stable acid
2. Atom size – acidity increases if atom size increases
3. Hybridization – acidity increases with more stable bonds (triple bond > double bond > single bond)
4. Resonance – a higher resonance (dislocation of electrons) implies a higher acidity.
5. Inductive effects – a lower electron density results in a higher acidity.

Summary Materials and Molecules based on lecture slides

E. Jurak

Polymers are long strings of repeated subunits (molecules), oligomers are strings with a few repeated subunits, monomers are single subunits.

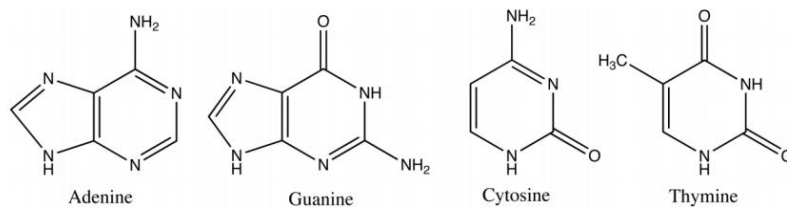
Three types of biomonomers (which can form oligomers and polymers):

1. Amino acids, which peptide bonds between monomers (suffix: -ine)
2. Saccharides, with glycosidic bonds between monomers (suffix: -ose)
3. Nucleotides, with phosphodiester bonds between monomers

The prefix of a compound changes, if it is an oligomer or polymer. For example, amino acid → oligopeptide → polypeptide.

DNA and RNA are nucleic acids. They function as informational molecules in cells. DNA passes from one generation to the other. RNA is a copy of the DNA. An arrangement of four letters, each representing an amino acid, provides a blueprint for every living organism on earth.

DNA-bases → the four “letters” (amino acids, A, G, C and T) existing in a DNA-strand:



Each DNA-base pairs up with another base forming a base pair. The base pairs are: G-C, A-T and A-U (uracil). Uracil occurs in RNA, not in DNA. So, within RNA, A attaches to U and T attaches to A. Within DNA, A attaches to T and T attaches to A. G and C will attach both in DNA and RNA the same. Bases are paired this way, because Guanine and Cytosine contain three OH-group, which can bind with each other. Adenine, Thymine and Uracil all contain only two OH-groups.

Cytosine, Uracil and Thymine are pyrimidines, which are smaller.

Nucleoside → (nitrogenous) Base + ribose or deoxyribose (both monosaccharides)

Nucleotide → a nucleoside joined to one or more phosphoryl groups by an ester linkage. Most commonly referred to as a nucleoside with the number of attached phosphoryl groups noted. DNA and RNA are built out of nucleoside triphosphates.

The carbon atoms in the ribose or deoxyribose are stated with numbers. The phosphoryl group attaches to the C-5'-atom and C-3'-atom. The nitrogenous base attaches to the C-1'-atom. Polymers and oligomers must be read from the 3' to 5' side (direction of the molecule).

De novo pathways → the framework of a pyrimidine base is assembled first and then attached to a ribose. The framework for a purine is synthesized piece by piece directly onto the ribose-based molecule.

Salvage pathways → Preformed bases are recovered and reconnected to a ribose unit.

Replication → DNA unwinds and at each separate string a new string attaches, making it two new DNA-strings

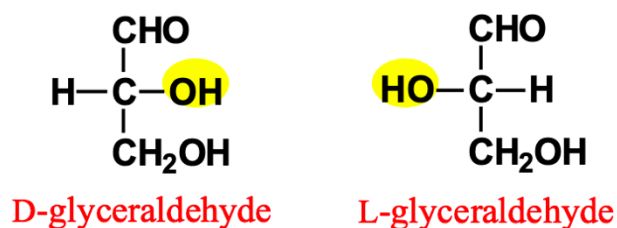
Transcription → The process in which a DNA-string is unwinded. This DNA-string is transcribed (copied) to messenger RNA (mRNA).

Translation → The mRNA, formed in transcription, is transported to the ribosome. This is done with the help of transfer RNA (tRNA). Three bases of the RNA are grouped together in groups of 3 (triplet/codon) which each represent a specific amino acid. By reading these codons, amino acids are put in sequence and a new polypeptide/protein is formed.

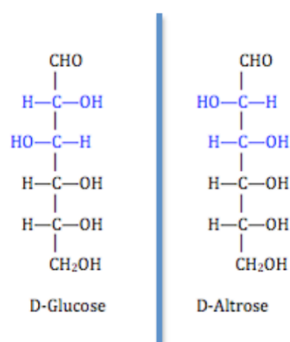
From DNA to protein: <https://www.youtube.com/watch?v=gG7uCskUOrA> Materials and Molecules 2019

Monosaccharides are colorless, crystalline solids. Hydrogen bonding is possible between the polar -OH groups and H₂O. Very soluble in water, but insoluble in non-hydroxylic solvents.

Levo (left) and Dexter (right) molecules → if the -OH group, attached to the bottom most asymmetric (second C from the bottom) is on the right then Dexter. If on the left, then Levo.
Example:



Diastereomers → certain molecules are not each other's mirror image. Example:



Fisher projection → Projection of a monosaccharide in which the carbon chain is written vertically with the most highly oxidized carbon atom at the top. Horizontal lines show groups projecting above the plane of the paper. Vertical lines show groups projecting behind the plane of the paper.

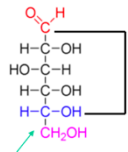
Haworth projection → A monosaccharide is shown as a cyclic structure. OH-groups which are on the right side in Fisher projection are below the cyclic carbohydrate. OH-groups that are on the left in Fisher projection are above the cyclic carbohydrate.

Alpha- and Beta- orientation → Alpha if the OH-group of the first carbon atom (C-1') is on the opposite side of the cyclic carbohydrate as the substituent on the fifth (C-5') carbon atom. Beta if they are on the same side.

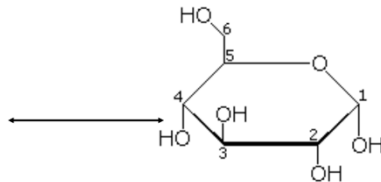
Chair projection → Monosaccharide is shown in the form of a “chair”.

Examples:

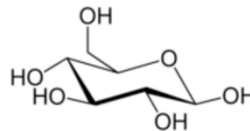
Fisher



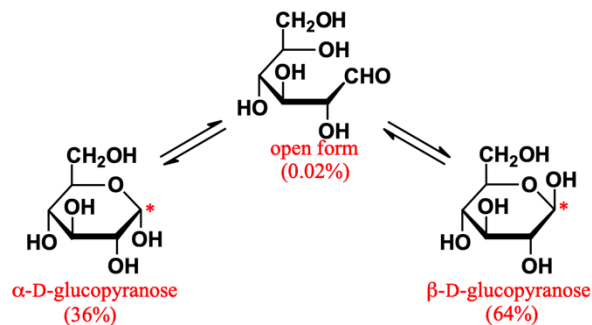
Haworth (alpha)



Chair



Mutarotation → alpha- and beta- anomers of polysaccharides are interconvertible in aqueous solutions, due to their op-chain aldehyde form. Example:



Pyranoses → six-membered hemiacetal rings, named after its heterocycle pyran. →



Furanoses → five-membered hemiacetal rings, named after its heterocycle furan. →



States of biomass: Primary biomass – created by photosynthesis. Secondary biomass – processed primary resources. Tertiary biomass – post-consumer residue streams.

Zwitterions → overall neutral molecules, but it contains charged ends (charge dislocation)

Amino acids and other biological compounds contain more than one pKa value. If the amino acid is acidic or basic depends on the pH of the solution.

Overall pKa of the molecule (pI): $pI = (pK1 + pK2 + \dots + pKn) / n$

Isoelectric point → pH at which there is no net charge.

Polymers are called peptides if it contains 2-50 individual amino acid units. They are called proteins, if it contains more than 50 individual amino acid units.

Peptide bonds are formed between the N-terminus (NH₂-side of the amino acid) and the C-terminus (COOH-side of the amino acid).

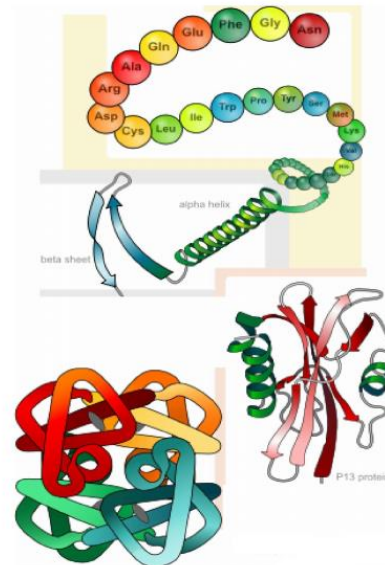
Levels of protein structures:

Primary: a sequence of amino acids

Secondary: sequences of amino acids are linked with hydrogen bonds

Tertiary: alpha helices and pleated sheets. Active form a protein

Quaternary: protein consisting of multiple amino acid chains



Recombinant protein → manipulated form of a protein

Plasmids → small pieces of DNA that replicate independently from a DNA-host

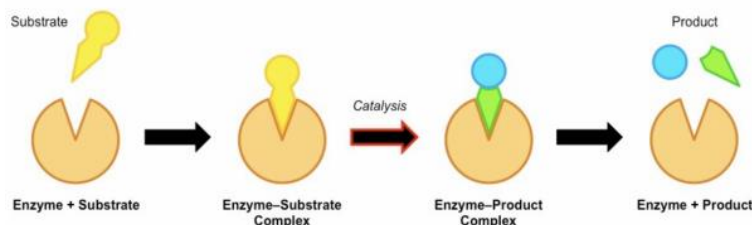
Chaperons → proteins that stimulate the folding of proteins.

Six classes of enzymes:

1. Oxidoreductase – transfers electrons between molecules
2. Transferase – transfers functional groups between molecules
3. Hydrolases – Cleave molecules by addition of water
4. Lyases – Add atom or functional groups to a double bond or remove them to form a double bond
5. Isomerases – Move functional groups within a molecule
6. Ligases – Joins two molecules at the expense of ATP hydrolysis

Denaturation → A protein loses its structure.

Lock and key principle → A substrate suits only on a specific corresponding enzyme. Example:



Induced fit → the enzyme mutates in shape to host the substrate

Enzyme catalysis → the increase in the rate of chemical reaction by active site of a protein

Enzyme inhibitor → a molecule which disrupts the normal reaction pathway between an enzyme and a substrate. Irreversible if the inhibition could not be undone.

Forms of inhibition:

1. Competitive inhibition – the substrate and the inhibitor compete for the same place in the enzyme.
2. Non-competitive inhibition – the inhibitor attaches to another part of the enzyme. Both, the inhibitor and the substrate are attached. Enzyme is then not active

Materials and Molecules (based on lecture slides)

BJ. Kooi

Properties of materials:

- Mechanical – strength, stiffness, hardness, etc.
- Electrical – conductivity
- Magnetic – hard and soft permanent magnets
- Thermal – heat conduction, expansion, etc.
- Optical – transparency for light with certain wavelength

Atoms bond because they have the natural tendency to form the electron configuration of the nearest noble gas. This tendency to attract another atom is measured in electronegativity. High electronegativity has the tendency to accept electrons. Low values give up electrons. (Elements increase in electronegativity from left to right in the periodic table)

Three types of chemical bonds (between atoms):

1. **Ionic:** atoms that have donated (positively charged) and atoms that accepted electrons (negatively charged) attract each other. (i.e. NaCl and MgO)
2. **Covalent:** atoms share their valence electron to bond (hybridization).
3. **Metallic:** valence electrons are delocalized from its atom-cores and can move freely through the metal. These electrons bond the remaining positively charged ion cores.

Van der Waals- force → the tendency of molecules to attract each other. Very weak compared to three bonds above.

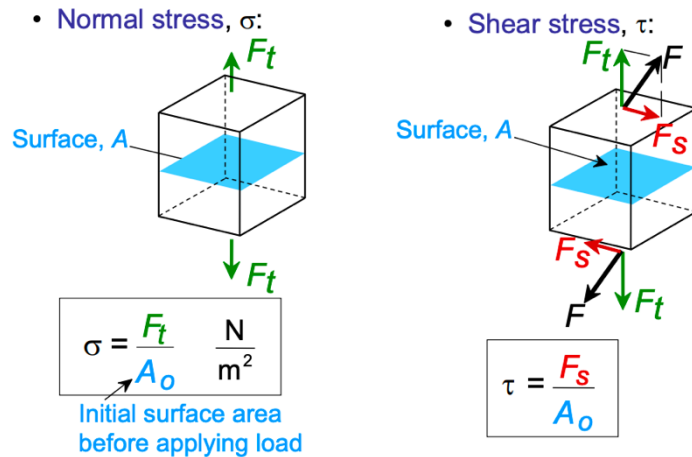
Within metallic elements, a bond with an element which differs greatly in electronegativity results in an ionic bond. A metallic element with an element with a small difference in electronegativity gives a covalent bond. A combination between two metallic elements always result in a metallic bond.

Properties of different bonds:

*exceptions are possible

Bonding	Metallic	Covalent	Ionic	v.d. Waals+ Covalent
Material	Metal	Ceramic/ Semiconductor	Ceramic	Polymer
Electrical Conduction	High	Low*	Low*	Low*
Thermal Conduction	High	Low*	Low	Low
Ductility	High*	Low	Low	High
Hardness	Low*	High	High	Low
Melting point	Low-High	High	High	Low*

Stress → the force divided by the (initial) surface area. Distinguish between normal and shear stress. Normal stress is perpendicular to the surface, shear stress encounters an angle.



Strain → Deformation of a material, relative to its length. $\varepsilon = \frac{l - l_0}{l_0}$

Tensile → Stretching something out, opposite is compressive

Shear → Force on a surface, applied with an angle

(Linear) elastic materials:

For (linear) elastic holds: if the stress disappears, the strain disappears as well

Young's modulus → A measure of stiffness with symbol E . $\varepsilon \parallel = \frac{\sigma}{E}$, $\varepsilon \perp = -\nu \frac{\sigma}{E}$

Poisson's ratio (ν) → the tensile force of a material. Constant for each material. Only applicable if the force is perpendicular on the surface.

Plastics:

For plastics holds: if the stress disappears, the non-elastic part of the strain remains. Atomic planes start to slide along each other. This is possible due to movement of dislocations. The highest stress possible without plastic deformation is called elastic limit. The stress at which yielding (bending) occurs is called yield strength.

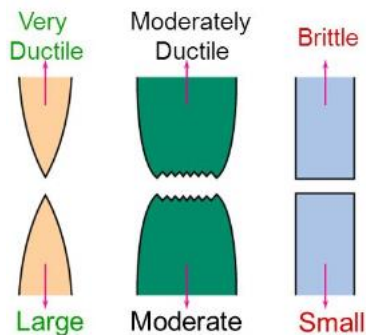
Failure:

The maximum stress a material can withstand is the tensile strength. When the tensile strength is reached, a decreasing load is needed for an increasing strain.

Necking → phenomenon that occurs when strain is suddenly increased greatly. The material then shows very rapid thinning and elongation.

The strain at which fracture occurs is called fracture strain. In case of tensile testing this is called elongation.

Ductility → A measure for fraction strain or elongation. A material is ductile if the fracture strain is much larger than the maximum elastic strain. A material is brittle if the fracture strain is mostly elastic.



Work/energy → energy stored in a material. Work to retrieve this energy from the material. Energy stored in the material is the surface below the stress-strain curve. $U = \int F ds = V_0 \int \sigma d\varepsilon$ with Toughness U. For elastics: $U_e = \frac{V_0}{2} \sigma \varepsilon = \frac{V_0}{2} * \frac{\sigma^2}{E}$

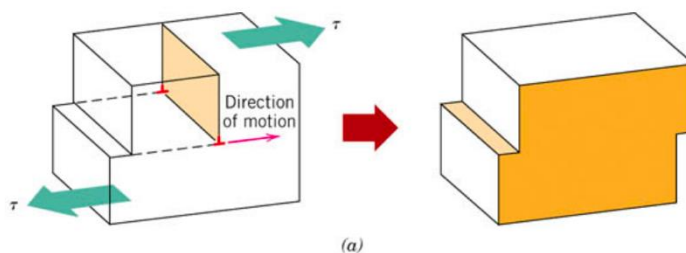
True stress → The actual stress, different from engineering stress. $\sigma_T = \sigma(1 + \varepsilon)$

True strain → The actual strain, different from engineering strain.

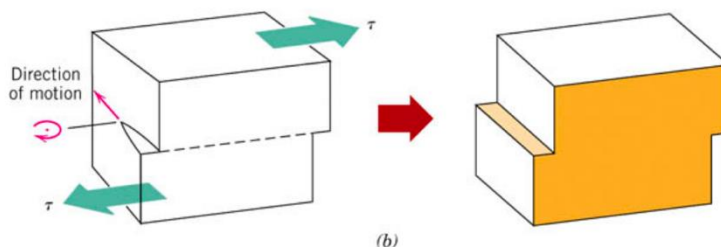
$$\varepsilon_T = \int_{l_0}^{l_i} \frac{dl}{l} = \ln\left(\frac{l_i}{l_0}\right) = \ln(1 + \varepsilon)$$

Hardness → Resistance against local plastic deformation. Tensile strength and hardness are often correlated.

Dislocations → Edge dislocation: displacements of half a crystal plane, Burgers vector perpendicular to the dislocation line. Screw dislocation: displacement of one crystal with every 360 turn. Burgers vector parallel to the dislocation line. Mixed is also possible.



Difference between dislocation type: edge (above) and screw (below)



Fatigue → due to a long time of force (stress cycle) on a material it gets fatigue (tired). This could break material.

Obstacles for dislocation movement:

1. **Other dislocations** – both repulsion and attraction
2. **Interstitial or substitutional atom** – likes to be in compressive- or tensile strain regions of dislocation and restricts further sliding of dislocations
3. **Grain boundaries**: by misorientation and disordered space between the grains crossing of dislocations is strongly restricted
4. **Precipitates**: slip can usually not occur through precipitate and will have to move around it.

All these obstacles reduce dislocation mobility, which leads to stronger and harder materials, but also more brittle materials.

Methods to strengthen materials:

1. **Cold work/hardening** – dislocation is brought to a higher density which increases strength. Also, more brittle (lower ductility)
2. **Add substitutional atoms** – add smaller atoms: smaller atoms prefer to be in compressive regions around dislocation, which hinder dislocation mobility. Add larger atoms: larger atoms prefer to be in tension regions around dislocation and hinder the dislocation mobility.
3. **Grain boundaries** – by disorientated and disordered space between the grains, further slip of dislocation is strongly hampered.
4. **Precipitates** – Many small particles provide more strength than large particles, since they have coherent interfaces. Mainly used in metal alloys.

Sizes of atoms and grains could be influenced by temperature.

Ohm's law: $V = IR$ (Voltage = Current x Resistance)

Resistivity (measurement of resistance) $\rho = \frac{RA}{l}$, with A cross-sectional area and l length of the wire.

Conductivity: $\sigma = \frac{1}{\rho}$

Conductivity and resistivity differ very much per element/material, due to the difference in number of free (=conduction) electrons n per unit volume. $\sigma = n|e|\mu_e$

How higher the density of free electrons, the more resistivity. Space between these electrons are stated as bandgaps. Band and bandgaps are visualized in band structures.

The resistivity of metals increases if the temperature increases.

$$\rho_{Thermal} \approx aT + b \quad (\text{pure metals } b \approx 0)$$
$$\rho_{Total} = \rho_{Thermal} + \rho_{Impurity} + \rho_{Deformation}$$

In semi-conductors the number of free electrons n is the same as the number of holes (bandgaps) p .

$$\sigma = n|e|\mu_e + p|e|\mu_h$$
$$\sigma \approx C_1 n = C_1 p = C_2 \exp\left(-\frac{E_g}{2kT}\right)$$

Intrinsic n-type semi-conductors: $n \gg p$, +1 element enters the semi-conductor

$$\sigma \approx C_a n = C_b \exp\left(-\frac{E_g - E_d}{kT}\right)$$

Intrinsic p-type semi-conductor: $p \gg n$, -1 element enters the semi-conductor

$$\sigma \approx C_c p = C_d \exp\left(-\frac{E_a}{kT}\right)$$

Material selection: Without shape

Performance: $P = F(f, g, m) = F(\text{functional requirements, geometric parameters, material properties})$
 Also separable in: $P = F_1(f) F_2(g) F_3(m)$

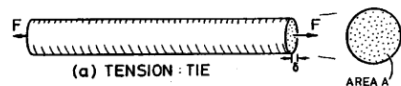
Functional requirements → the requirements in terms of function, such as safety factors and safe design

Geometric parameters → Geometric parameters, such as length, height and area

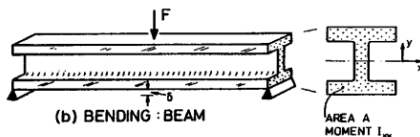
Material properties → Properties of a material, such as mass, density and stiffness.

Material selection: With shape

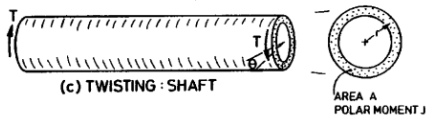
Standard structural members in design. Overview if shape/area matters for loading:



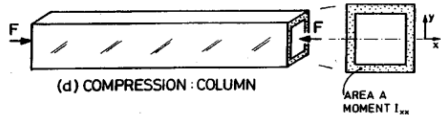
Area A matters,
not shape!!!



Area A and
shape I_{xx} matter



Area A and
shape J matter



Area A and shape I_{min} matter
in case of buckling; with
pure compression shape
does not matter!

Shape factor ϕ → A measurement for the efficiency gain by shaping. $\phi = \frac{4\pi I}{A^2}$

Shape factor could be divided in two different kinds, Bending and Torsion. The higher the shape factor, the higher the efficiency of shaping this material.

$$\text{Bending: } \phi_B^e = \frac{4\pi I_{xx}}{A^2} = \frac{4\pi}{A^2} \int y^2 dA \quad \text{Torsion: } \phi_T^e = \frac{2\pi J}{A^2} = \frac{2\pi}{A^2} \int r^2 dA$$

With y is the distance of the bending axis and r is the length of the rotation axis (distance to the rotation centre)