

8. Water and Hydrogen Peroxide

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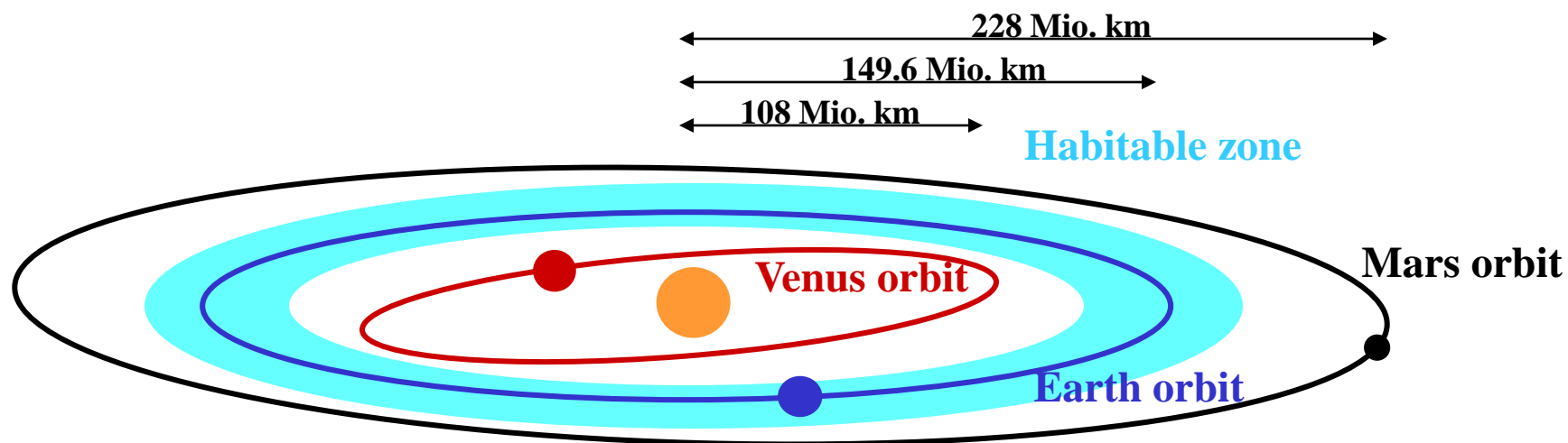
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8.1 Water – The Elixir of Life

Liquid Water is the Medium for Biological Processes (Biochemistry)

In a certain distance to a star a spherical shell exists, where liquid water can exist on a planet
⇒ habitable zone



Earth does circulate within that spherical shell around its central star (sun), so that most of its surface water is liquid. In contrast to that on Venus and Mars no liquid water exists.

8.2 Occurrence

Water exists on Earth in all physical States

Solid	Cryosphere (Antarctica, Greenland, high mountains)	2.6%
Liquid	Hydrosphere (oceans, inner seas)	97.4%
Gaseous	Atmosphere	0.001% (25 mm)

**Water reserve on earth $\sim 1.38 \cdot 10^{18} \text{ m}^3$
→ $d \sim 2700 \text{ km}$**

Surface area of earth $\sim 510 \cdot 10^{12} \text{ m}^2$

**Additionally, water exist in bound form as crystal water and solvent in all living beings
(plants, animals, microorganisms)**

Lithosphere

Biosphere

(water from space $\sim 2 \text{ mio. tons/year}$)

All life processes need aqueous environments, i.e. biology can also be called **aqueous chemistry**

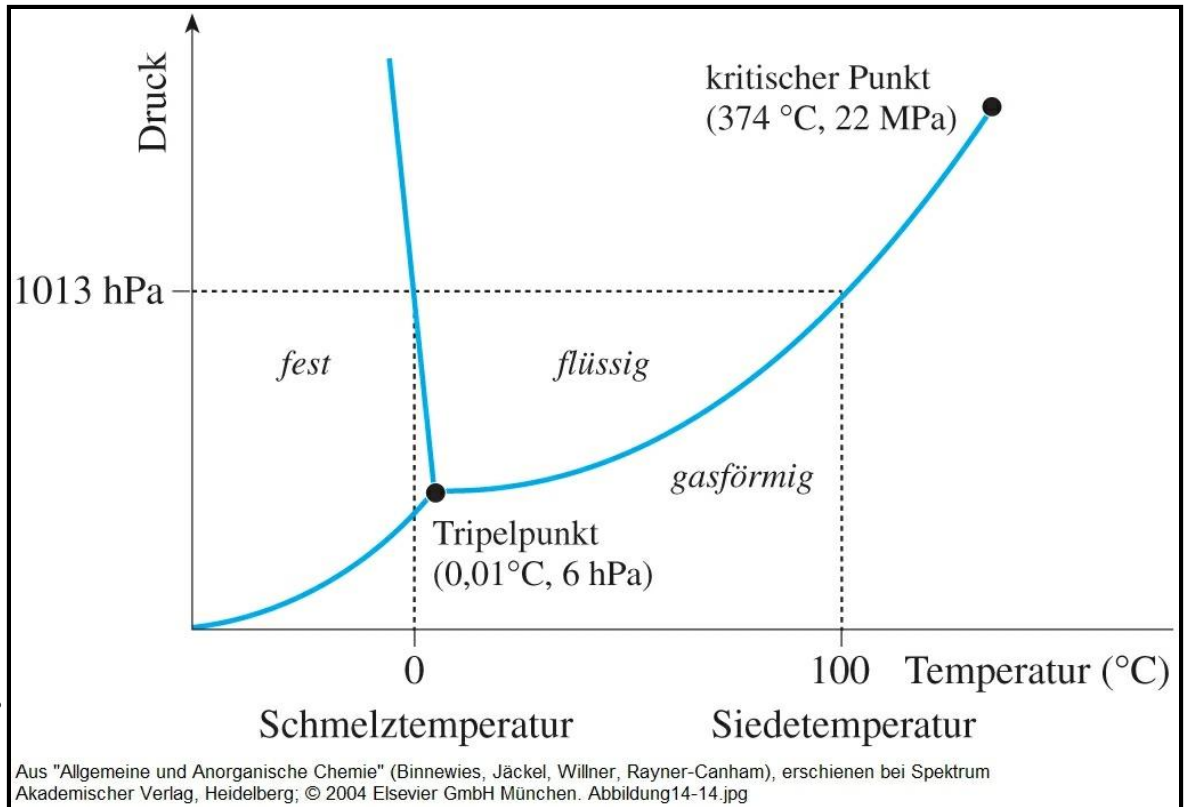
Human body $65\% \text{ H}_2\text{O}$

Several kinds of vegetables $90\% \text{ H}_2\text{O}$

8.3 Physical Properties

In highly pure State, Water is a clear, odour- and tasteless, transparent Substance

- **Melting point: $0\text{ }^{\circ}\text{C} = 273.15\text{ K}$**
- **Boiling point: $100\text{ }^{\circ}\text{C} = 373.15\text{ K}$**
- **High transparency between 190 and 800 nm**
- **Impurities or defects can lead to colouring**
 \Rightarrow blue ice in glaciers
- **The state variables pressure and temperature determine, whether H_2O exists as solid ice, liquid water or vapour**



8.3 Physical Properties

Some important Physical Parameters of Water

Parameter	Symbol	Value	Unit	Remark
Density	ρ	≤ 1	g cm^{-3}	Density anomaly !
Specific heat capacity	c_p	4216	$\text{J kg}^{-1} \text{K}^{-1}$	Very high!
Heat of evaporation at RT	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$	$2,495 \cdot 10^6$	J kg^{-1}	$2,5001 \cdot 10^6$ at $0 \text{ }^{\circ}\text{C}$ $2,26 \cdot 10^6$ at $100 \text{ }^{\circ}\text{C}$
Heat of fusion	$\Delta_{\text{l}}^{\text{s}}H_{\text{m}}$	$3,3 \cdot 10^5$	J kg^{-1}	
Surface tension	σ	0,076	$\text{N m}^{-1} = \text{J m}^{-2}$	at $0 \text{ }^{\circ}\text{C}$

8.4 Structure

The unique Properties of Water can be Traced back to the Structure of the H₂O-Molecules and the Different EN-Values of the Bonding Partners

1. Highly polarized O-H bonds lead to a molecule with high dipole moment
 $\Rightarrow \mu = q \cdot d = 1.85 \text{ Debye} \Rightarrow$ high polarity and strong hydrogen bonds

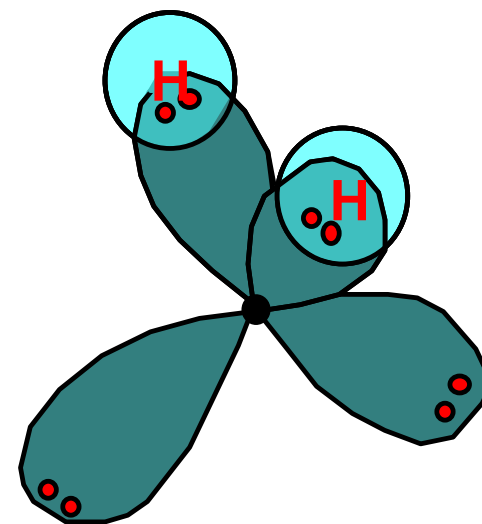
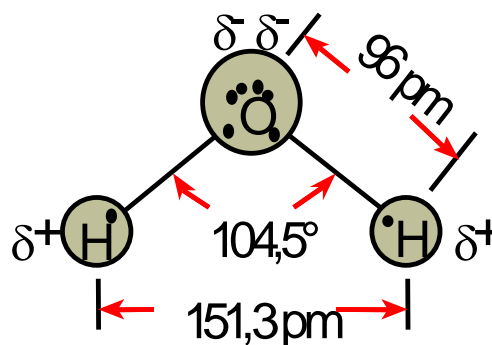
2. Formal hybridisation of the atomic orbitals of oxygen to four energetically degenerate hybrid orbitals



2 x sp^3 bond to hydrogen

2 x sp^3 non-bonding

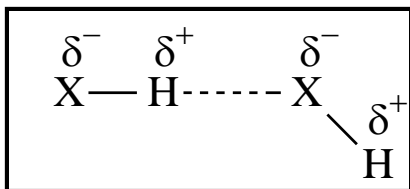
\Rightarrow angled structure with small deviation from tetrahedron angle



8.4 Structure

Hydrogen Bonds between HX-Molecules (X = N, P, O, S, F, Cl)

Between the positively charged H-atoms of the HX molecule and the free electron pair of a X-atom of a neighbouring molecule electrostatic attraction exists



X = F, O, N \Rightarrow strong hydrogen bonds

X = Cl, S, P \Rightarrow weak hydrogen bonds

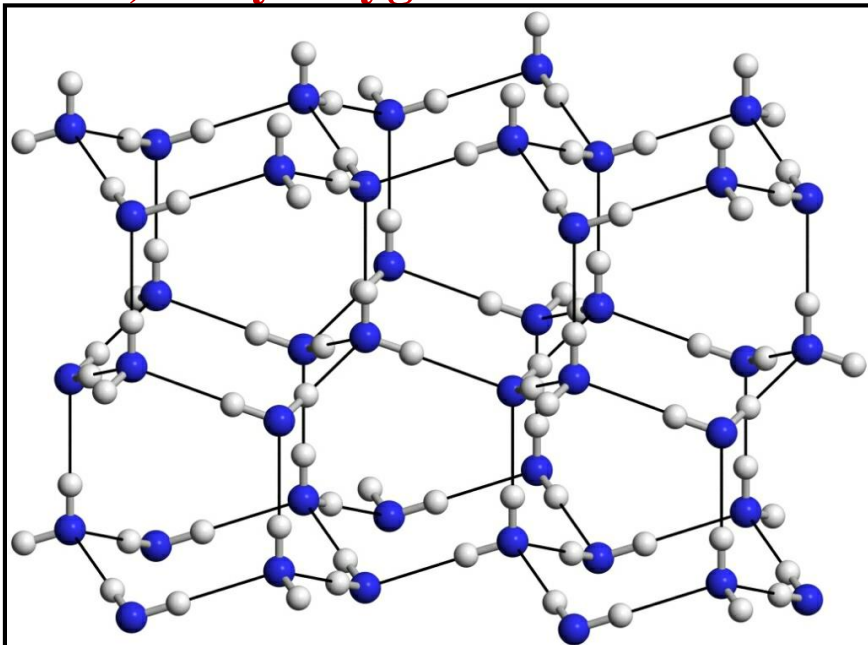
Hydrogen bonds **X–H \cdots X** are usually arranged linearly, since then the attraction **H \cdots X** is strongest and the repulsion between the X-atoms is smallest

Liquid water \Rightarrow each **H₂O** molecule is connected to **3 – 4** neighbouring atoms via hydrogen bonds

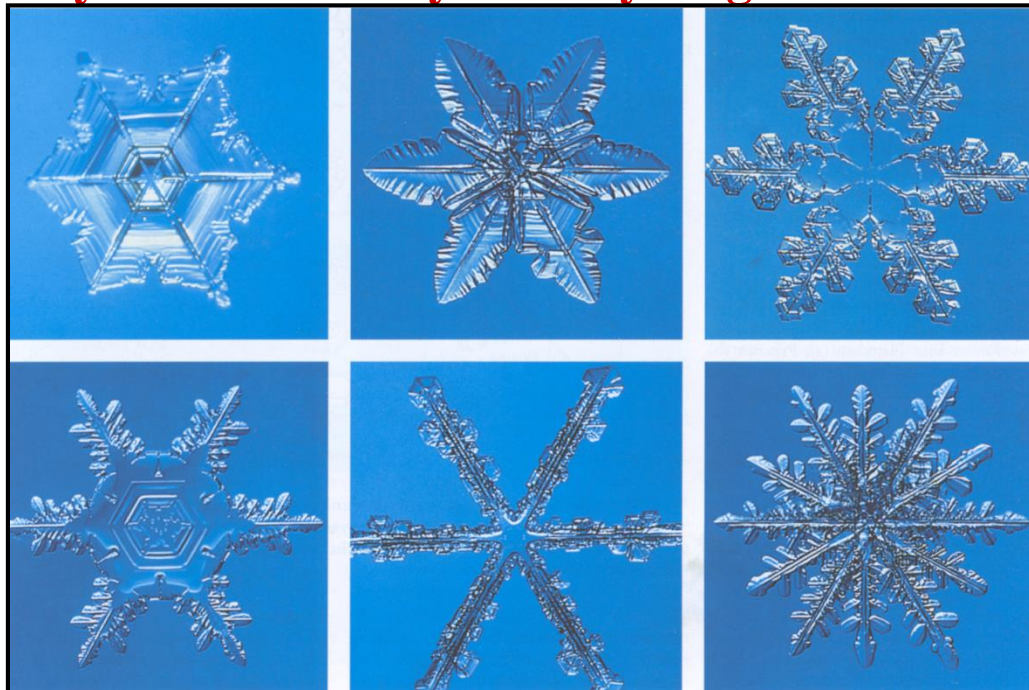
Solid water (ice) \Rightarrow each **H₂O** molecule is connected to **4** neighbouring molecules via hydrogen bonds

8.4 Structure

In Ice, every Oxygen Atom is Tetrahedrally coordinated by four Hydrogen Atoms



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Temperature [°C] Density [g/ml]

0 (ice)	0.9168	⇒ Open, hexagonal structure with cavities
0 (water)	0.99984	⇒ Decrease of volume during melting!
4	1.000000	⇒ Density anomaly of water
10	0.99970	⇒ above 4 °C thermal increase of volume
20	0.99821	

8.5 Water as Solvent

The Reason why Water is such a good Solvent for Compounds based on polar Molecules, such as Sugars or ions (Salts), is that it exhibits Dipole Characteristics and is able to form Hydrogen Bonds



Dissolved ions in water are always hydrated (aq)

- \Rightarrow Depending on their ionic charge density they are typically coordinated by four to six H_2O -molecules
- \Rightarrow Water lowers the strength of electrostatic interactions compared to the state in vacuum by the factor of 80 (dielectric constant $\epsilon_r = 80$)

Hydration of salts can be either exo- or endothermic:



8.6 Water as Medium for Electrolytes

Electrolytes are Compounds that dissolve into free mobile Ions in Water

1. Ionic compounds

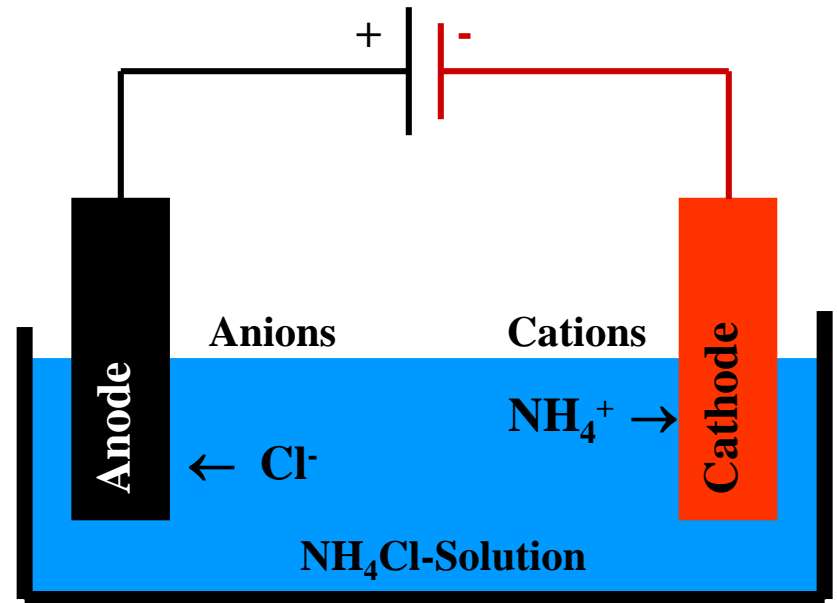


2. Highly polar, covalent compounds



⇒ **Formation of free mobile ions**

⇒ **Facilitation of electricity transmission, i.e. increase of electric conductivity**



In contrary to that, substances such as sugars or alcohols, which form aqueous solutions that are not conductive, are called non-electrolytes

8.6 Water as Medium for Electrolytes

Conductivity of aqueous Solutions of several Compounds

$$\kappa = \frac{1}{R} \cdot \frac{1}{q} [\mu\text{S} / \text{cm}] \quad \text{with } R = \text{electric resistance, } q = \text{distance of panels}$$

<u>Solution</u>	<u>κ</u>	<u>Explain</u>
Distilled water	13	Auto-protolysis of H_2O + dissolved CO_2 $2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+$
NaCl (c = 0.1 mol/l)	10620	Strong electrolyte
D-glucose (c = 0.1 mol/l)	14	Non-electrolyte (auto-protolysis of H_2O + dissolved CO_2)
HCl (c = 0.01 mol/l)	24300	Strong electrolyte + high ionic mobility
CH_3COOH (c = 0.1 mol/l)	522	Weak electrolyte

8.6 Water as Medium for Electrolytes

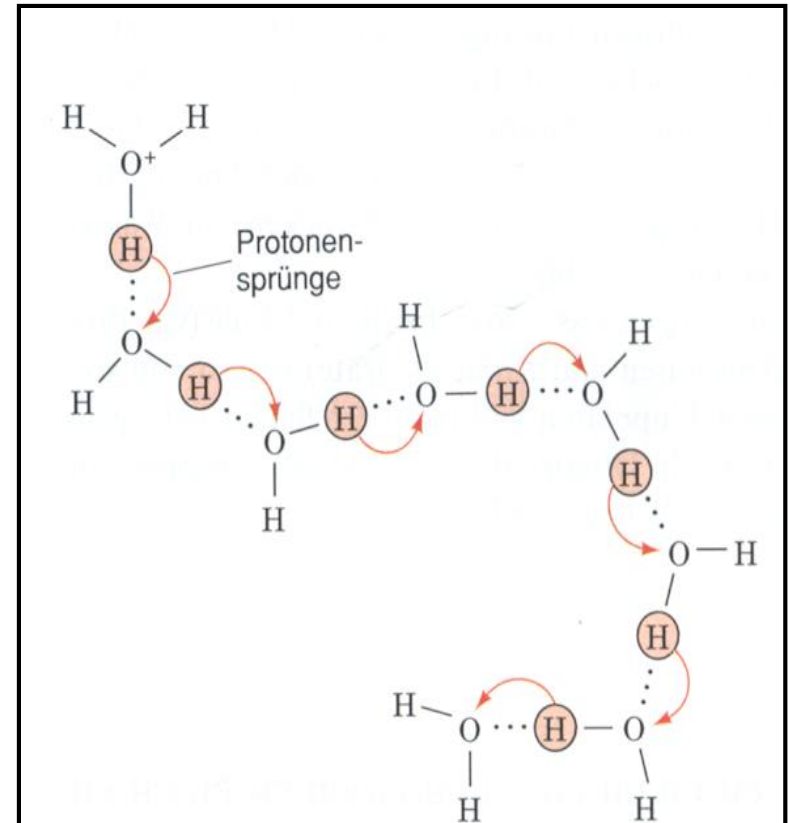
Ionic Mobility in aqueous Solutions at 298 K

Ion	Mobility [10^{-5} in $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$]
H_3O^+	362.4
Li^+	40.1
Na^+	51.9
K^+	76.1
NH_4^+	76.0
Mg^{2+}	55.0
Ca^{2+}	61.6
OH^-	197.6
Cl^-	76.3
Br^-	78.3
CH_3COO^-	40.9
SO_4^{2-}	79.8

The high proton conductivity is crucial for a number of bio-chemical reactions

⇒ transmembrane protonic pumps

Mechanism of proton jumps for hydronium ions in aqueous solution

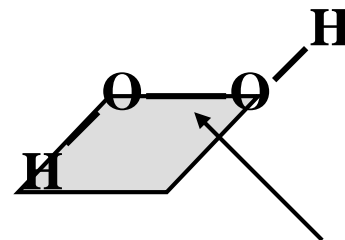


8.7 Hydrogen Peroxide

Pure H₂O₂ is a light blue Liquid of high Viscosity

Structure

Two OH-units, arranged under an angle, the dihedral angle, of 111°

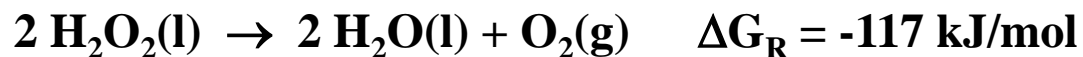


Long O-O bond

“predetermined breaking point” → 2 OH·-radicals

Reactivity

- H₂O₂ is thermodynamically unstable



- To customary solutions of 30 – 35% of H₂O₂ in H₂O stabilizers are often added to slow down decomposition
- Decomposition is catalysed by metals, dust, blood, light, metal oxides etc.
- Strong oxidising agent
- The peroxide anion, O₂²⁻, is a strong base:



9. Ionic Bond and Salts

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9.2 Ionic radii

9.3 Polarisation and covalence

9.4 Hydration of ions

9.5 Ionic structures

9.6 Lattice energy of ionic crystals

9.7 Nomenclature of salts

Rock salt, NaCl



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Sylvine, KCl



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9.1 Properties of Ionic Compounds

Ionic Compounds are formed by the Combination of highly metallic Elements with highly non-metallic Elements

Metallic character and radii decrease

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															

Metallic character
and radii increase

In ionic bonds electrons are formally attributed to one sort of atoms:



9.1 Properties of Ionic Compounds

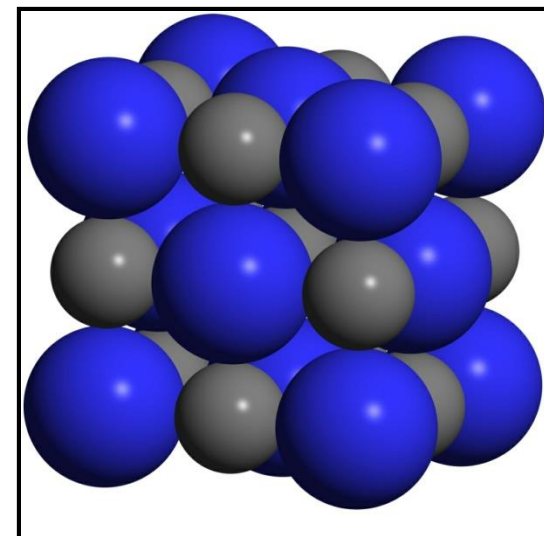
Typical ionic Compounds are Alkaline Metal Halides, e.g. Rock Salt, NaCl

Macroscopic properties

- **Hard and brittle solids (crystals built up from ion)**
- **High melting points**
- **Poor electric conductivity**
- **Melt exhibits high electric conductivity**
- **(Good) solubility in polar solvents (H_2O)**
- **Solutions are electrically conductive**

Structural build-up

- **Made of spherical cations and anions**
- **Bonding forces show no direction**
- **The ions try to reach an as dense as possible configuration where every ion is surrounded by as many ions of opposite charge as possible**



9.2 Ionic Radii

The ionic Radius depends on the Strength of the Core-Electron-Interaction

Trends

- Cation tend to be smaller than anions
- Within the main groups the ionic radius increases with growing atomic number



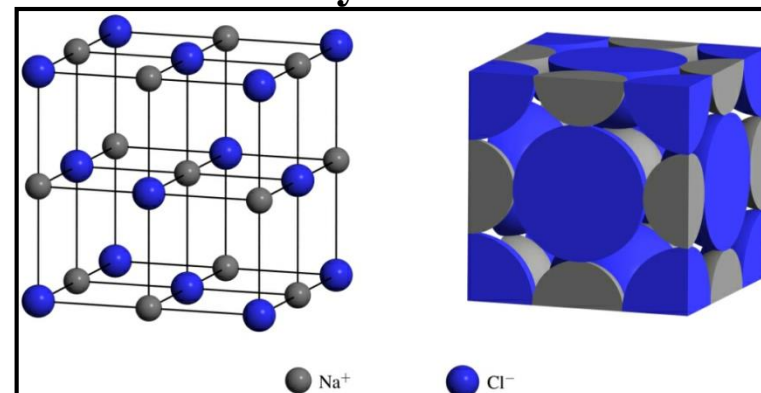
- For ions with the same electronic configuration the radius decreases with increasing atomic numbers



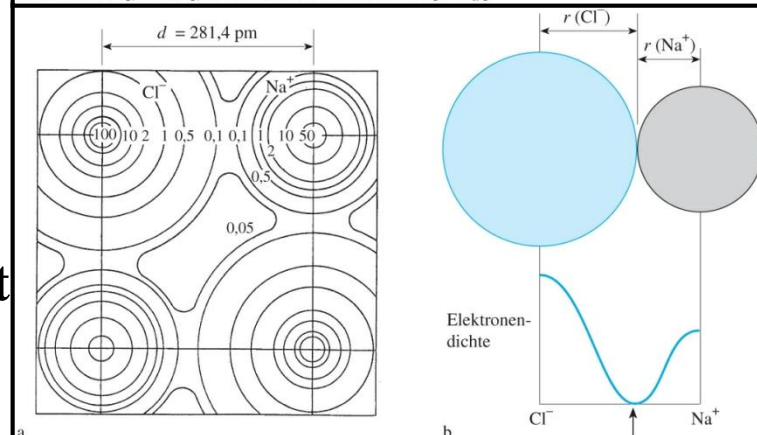
- If there are several valence states for an element the radius decreases with increasing charge



NaCl crystal structure



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9.3 Polarisation and Covalence

Cations attract the Electrons of the Anions, so that the Anions get distorted (polarized) \Rightarrow Covalence or Covalent Bonding Character

Fajan's rule for polarisation

1. Cations are the more polarizing the smaller and the more charged it is
2. Anions can be polarized the easier the bigger and the more charged they are
3. Polarisation preferably takes place by cations which exhibit no noble gas configuration

Quantity for Polarisation strength

$$\text{Charge density} = \frac{\text{Ionic charge}}{\text{Ionic volume}} = \frac{\text{Nominal charge} \cdot 1.602 \cdot 10^{-19} [\text{C}]}{\frac{4}{3} \pi \cdot \text{Ionic radius}^3 [\text{mm}^3]}$$

<u>Ion</u>	<u>r [pm]</u>	<u>[C/mm³]</u>
Na ⁺	102	36
Al ³⁺	54	729

(true for coordination number 6)

9.4 Hydration of Ions

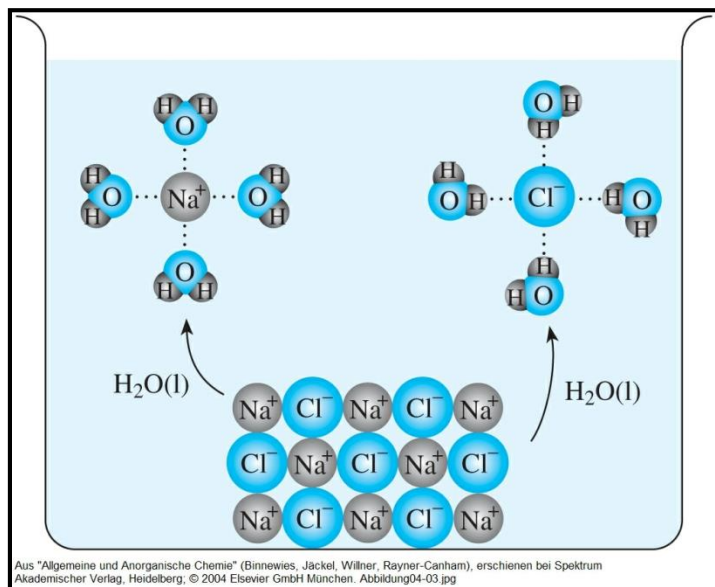
For Stabilisation Reasons Ions with High Charge Density are being solvated or hydrated in Water

Processes during dissolution of salts in water

a) NaCl



b) $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$



Al^{3+} exhibits such a high charge density that is hydrated even in its solid state



Hydration:

Ion/Dipole interaction

(The H_2O -molecule is a strong dipole!)

9.5 Ionic Structures

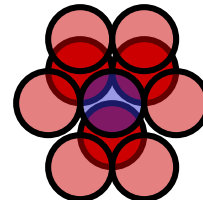
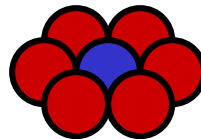
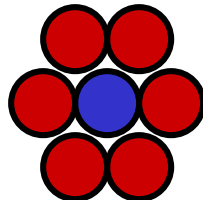
The spherical Ions always try to reach an as dense as possible Configuration and to minimize the Repulsion between ions of the same Charge

In general, cations are smaller than anions, so that the coordination conditions within the lattice is determined by the coordination number, CN, of the cation (number of surrounding anions).

⇒ CN depends on ratio of radii $r_{\text{cation}}/r_{\text{anion}}$

<u>Ratio of radii</u>	<u>CN</u>	<u>Geometry of configuration</u>
1	12	Cuboctahedron
0.732 - 0.999	8	Cube
0.414 - 0.732	6	Octahedron
0.225 - 0.414	4	Tetrahedron

$$r_{\text{cation}}/r_{\text{anion}} = 1$$

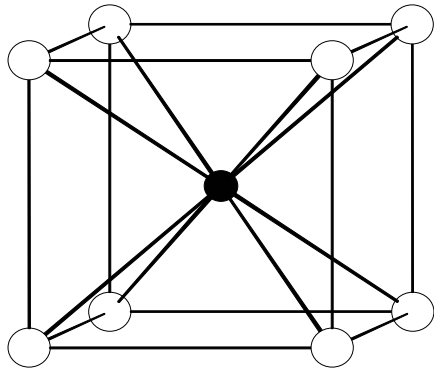


Anions “touch” each other in cuboctahedrons!

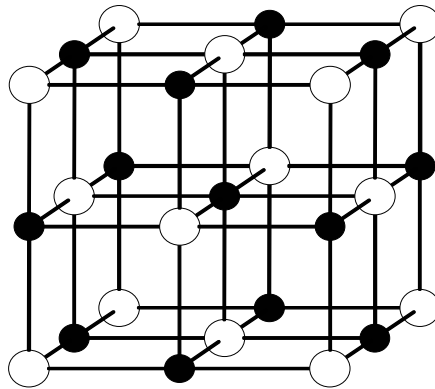
9.5 Ionic Structures

Most important Structural Prototypes of the Composition AB

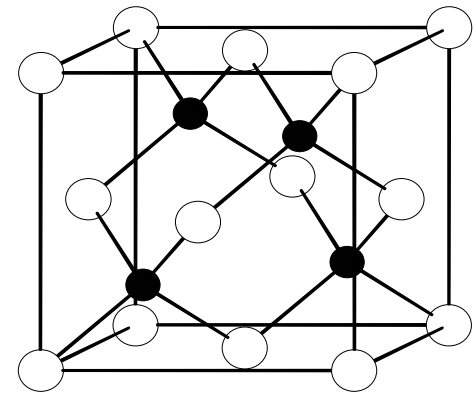
The coordination number of a cation depends on the ratio of the radii, r_K/r_A



CsCl (CN: 8)



NaCl (CN: 6)

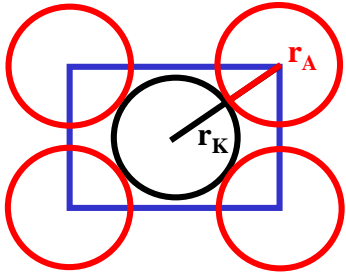


ZnS (CN: 4)
zinc blende

The critical ratio of radii, r_K/r_A , must not be exceeded or been fallen short of!

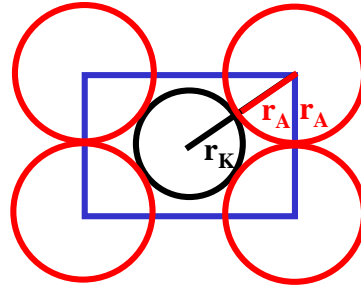
9.5 Ionic Structures

For $r_C/r_A > 0.732$ the Caesium Chloride Structure Type (CsCl-Lattice) occurs



Anions do not touch each other

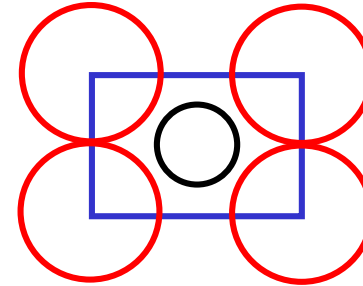
$$r_K/r_A = 1$$



Anions do touch each other

$$(r_K + r_A)/r_A = \sqrt{3}/1$$

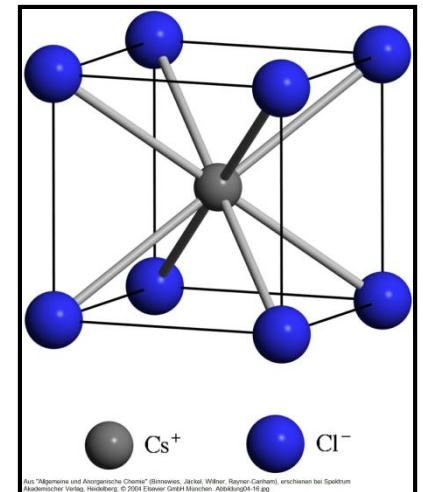
$$r_K/r_A = \sqrt{3}/1 - 1 = 0.732$$



Anions can not approach the cation any further

$$r_K/r_A < 0.732$$

<u>Example</u>	<u>r_K/r_A</u>
CsCl	0.94
CsBr	0.87
TlCl	0.83
CsI	0.79



9.5 Ionic Structures

For $0.414 < r_C/r_A < 0.732$ the Cation is coordinated octahedrally

The structure type in this case depends on the packaging of the anions

Anion packaging

Layer sequence

Structure type

hexagonal-dense

ABABAB

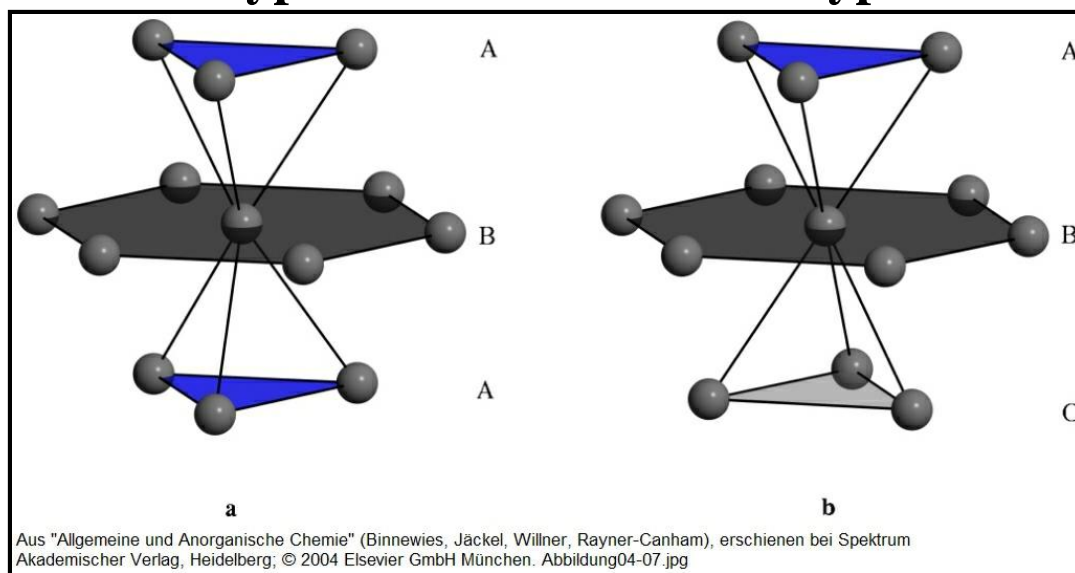
NiAs-type

cubic-dense

ABCABCABC

NaCl-type

Example	r_C/r_A
KBr	0.71
KI	0.64
NaCl	0.56
NaBr	0.52
NaI	0.47



9.5 Ionic Structures

For $r_C/r_A < 0.414$ the Cation is coordinated tetrahedrally

The structure type in this case depends on the packaging of the anions, again

Anion packaging

Layer sequence

Structure type

cubic-dense

ABCABCABC

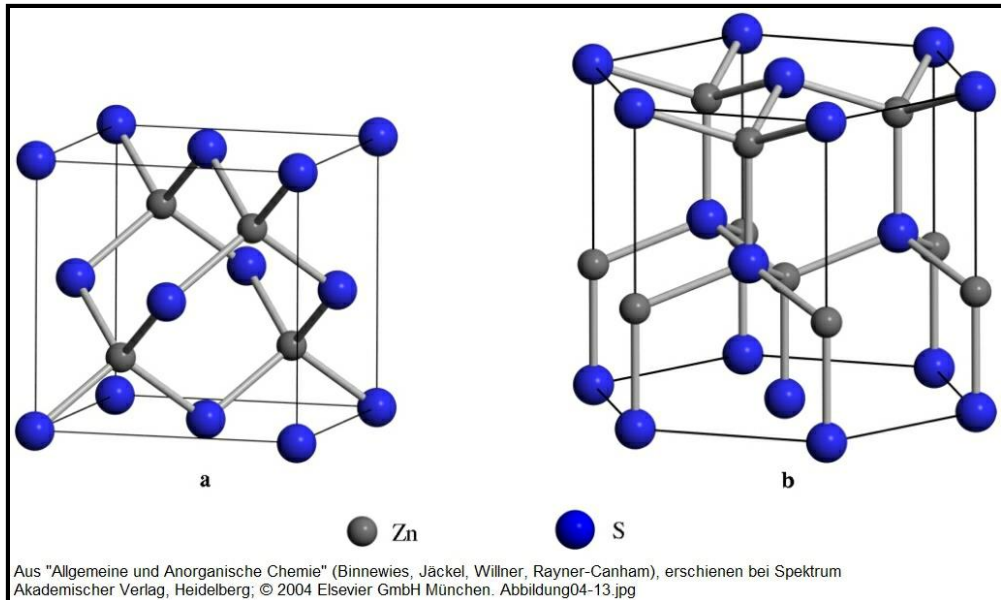
Zinc blende-type

hexagonal-dense

ABABAB

Wurtzite-type (ZnS)

<u>Example</u>	<u>r_C/r_A</u>
BeO	0.25
BeS	0.19



9.6 Lattice Energy of Ionic Crystals

The Lattice Energy of Crystals is the Amount of Energy which is released, when Ions from an infinite Distance Approach each other and are being combined to ionic Crystals

An ionic pair possesses an electrostatic potential energy which depends on charge and distance \Rightarrow Coulomb-energy

Example: NaCl-crystal: $z_C = -z_A$

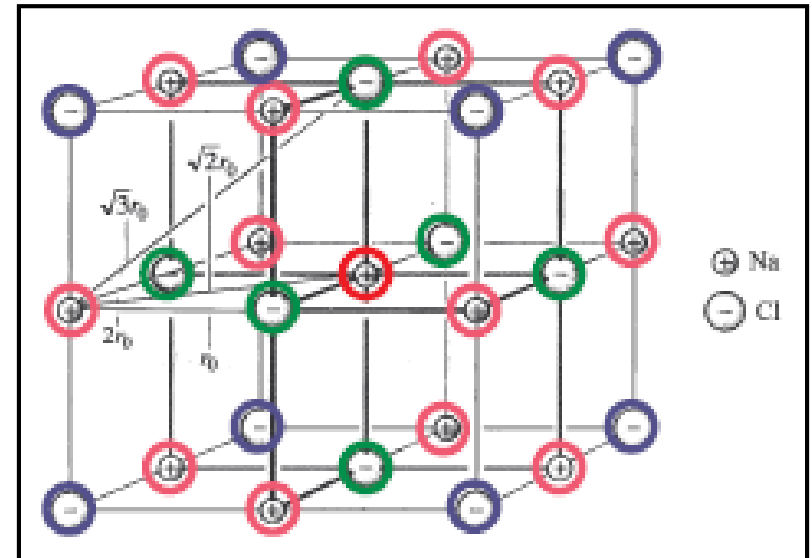
Na⁺-ion

- 6 negative neighbours with distance r
- 12 positive neighbours with distance $\sqrt{2}r$
- 8 negative neighbours with distance $\sqrt{3}r$
-

$$\Rightarrow E_C = -\frac{z_K^2 \cdot e^2}{4\pi \cdot \epsilon_0 \cdot r} \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \dots \right)$$

Geometrical term A

$$E_C = \frac{z_K \cdot z_A \cdot e^2}{4\pi \cdot \epsilon_0 \cdot r}$$



9.6 Lattice Energy of Ionic Crystals

The Limit of Convergence of the Geometrical Term is called the Madelung Constant, A (Characteristic for each Structure Type)

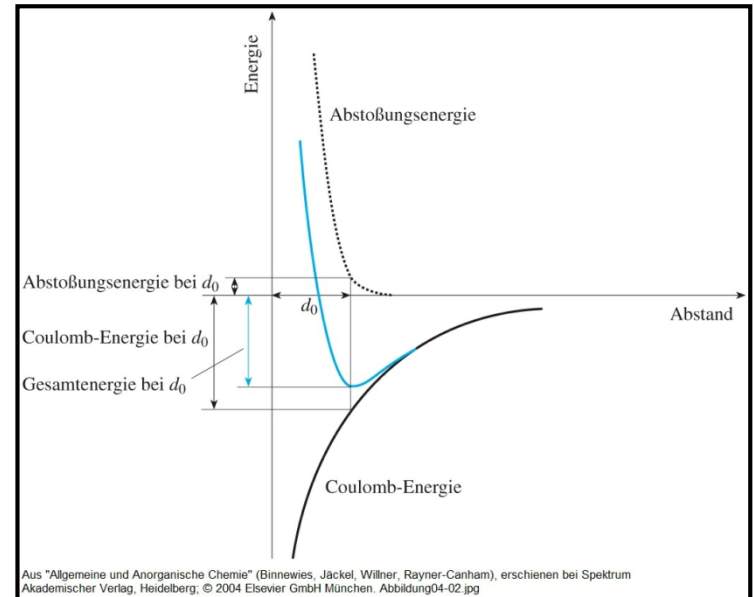
$$E_C = -\frac{z_K \cdot z_A \cdot e^2}{4\pi \cdot \epsilon_0 \cdot r} \cdot A \cdot N_A$$

Coulomb-energy for 1 mol (N_A) atoms

<u>Structure type</u>		<u>Madelung constant A</u>
CsCl	AB	1.7627
NaCl	AB	1.7476
Wurtzite	AB	1.6413
Zinc blende	AB	1.6381
Fluorite	AB ₂	5.0388
Rutile	AB ₂	4.8160
Corundum	A ₂ B ₃	25.0312

Lattice energy U_g

= Coulomb-energy + repulsive energy



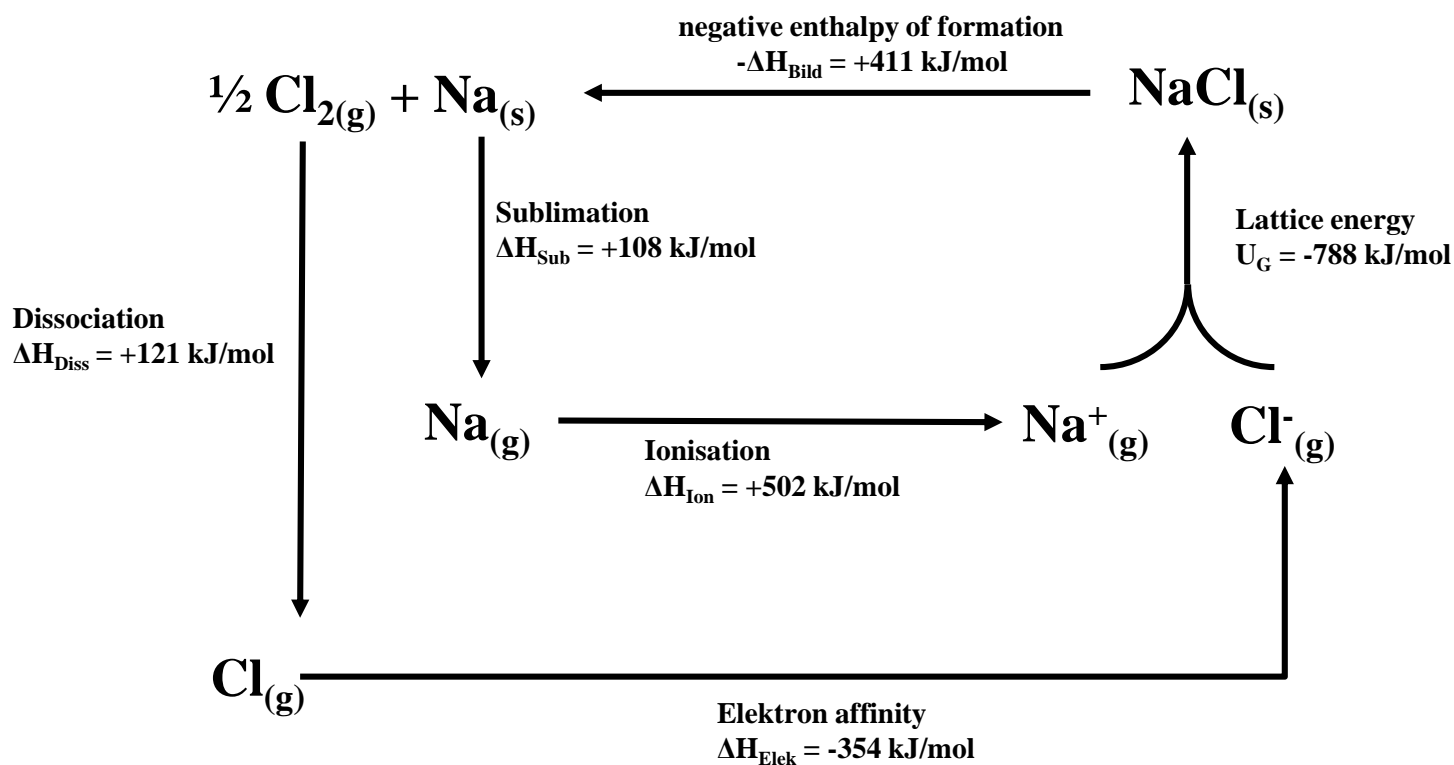
$$U_g = -\frac{z_K \cdot z_A \cdot e^2}{4\pi \cdot \epsilon_0 \cdot r} \cdot A \cdot N_A + \frac{B}{r^n}$$

B, n = constants

9.6 Lattice Energy of Ionic Crystals

Born-Haber Cycle

Example: Formation of NaCl (rock salt)



9.7 Nomenclature of Salts

Name of Salt = Cation Name + Anion Name

Creation of cation name

Mono atomic

Metal name + oxidation state

Cu⁺ copper(I)

Cu²⁺ copper(II)

multi atomic

suffix “-onium”

NH₄⁺ Ammonium

PH₄⁺ Phosphonium

Creation of anion name

Mono atomic

Element name + suffix(“-ide“ or “ite” or “ate”)

N³⁻ Nitride

P³⁻ Phosphide

As³⁻ Arsenide

Sb³⁻ Antimonite

S²⁻ Sulphide

multi atomic

CN⁻ Cyanide

CO₃²⁻ Carbonate

ClO₄⁻ Perchlorate

CrO₄²⁻ Chromate

SO₃²⁻ Sulphite

10. Atomic Bond

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10.8 Hydrogen Bonds

10.9 Valence Bond Theory

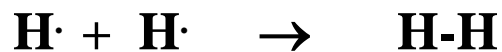
10.10 Molecular Orbital Theory

10.11 Nomenclature of Binary Molecular Compounds

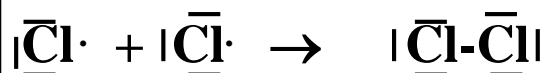
10.1 General Remarks

Atomic Bonds (Covalent or Homo-polar Bonds) are directed Interactions between Atoms with an high Electronic Density between the Atoms

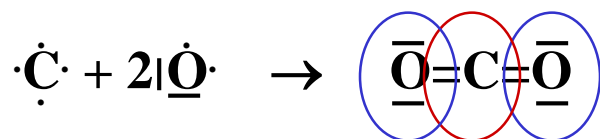
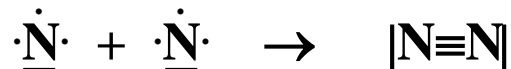
It is formed, when non-metals form a chemical bond with one another under the formation of a molecule:



“Principle of electron pair bond “



Mutual electron pairs are accounted to both bonding partners



Through the bonding of unpaired electrons single, double or triple bonds can be formed

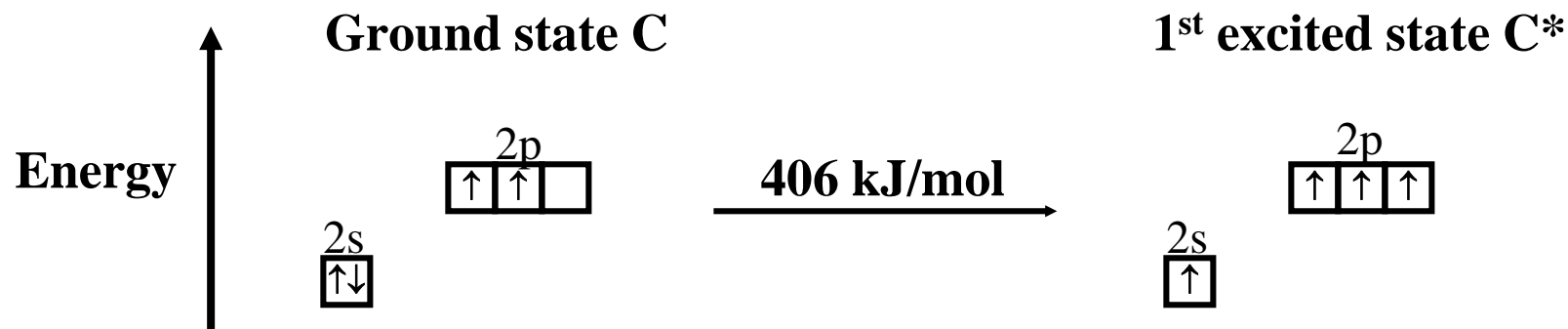
10.2 Lewis-Concept

Lewis-Theory States that every Atom in a Molecule strives to reach Noble Gas Configuration to become stable

Hydrogen	He-Configuration			
Other elements	Ne/Ar/Kr/Xe-configuration			⇒ Octet rule
Main group	4	5	6	7
2. Period	C	N	O	F
3. Period	Si	P	S	Cl
Electronic configuration	$\begin{array}{c} \text{s} \\ \boxed{\uparrow\downarrow} \end{array} \quad \begin{array}{c} \text{p} \\ \boxed{\uparrow} \boxed{\uparrow} \boxed{} \end{array}$	$\begin{array}{c} \text{s} \\ \boxed{\uparrow\downarrow} \end{array} \quad \begin{array}{c} \text{p} \\ \boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow} \end{array}$	$\begin{array}{c} \text{s} \\ \boxed{\uparrow\downarrow} \end{array} \quad \begin{array}{c} \text{p} \\ \boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\uparrow} \end{array}$	$\begin{array}{c} \text{s} \\ \boxed{\uparrow\downarrow} \end{array} \quad \begin{array}{c} \text{p} \\ \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow} \end{array}$
Potential bonds	2 (4)	3	2	1
Simple hydrogen Compounds	CH ₄ SiH ₄	NH ₃ PH ₃	H ₂ O H ₂ S	HF HCl

10.2 Lewis-Concept

The Ability of Carbon to form four Bonds is due to the Electronic Excitation of one 2s-Electron



Atom/Ion	Electronic configuration			Bonds	Outer electrons in bonding state	Example
	1s	2s	2p			
Li	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow}$	$\boxed{}\boxed{}\boxed{}$	1	2	LiH
Be*	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow}$	$\boxed{\uparrow}\boxed{}\boxed{}$	2	4	BeCl ₂
B*	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow}$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{}$	3	6	BF ₃
B ⁻ , C*, N ⁺	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow}$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$	4	8	BF ₄ ⁻ , CH ₄ , NH ₄ ⁺
N, O ⁺	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$	3	8	NH ₃ , H ₃ O ⁺
O, N ⁻	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$	2	8	H ₂ O, NH ₂ ⁻
O, F	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$	1	8	OH ⁻ , HF
O ²⁻ , F ⁻ , Ne	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$	0	-	-

10.2 Lewis-Concept

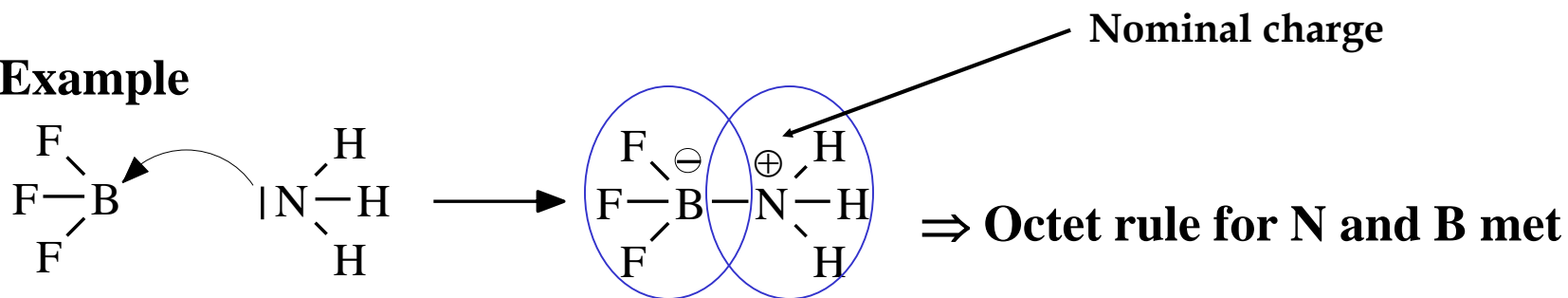
**Elements of the third or higher Period obey the Octet Rule, if only s- and p-Orbitals contribute to the Bond. Although also d-Orbitals may take part in Bonding
⇒ 18-Electron Rule**

Atom/Ion	Electronic configuration			Bonds	Outer electrons in bonding state	Example
	3s	3p	3d			
Na	↑	□ □ □	□ □ □ □ □	1	2	-
Mg*	↑	↑ □ □	□ □ □ □ □	2	4	-
Al*	↑	↑ ↑ □	□ □ □ □ □	3	6	AlCl ₃
Si*	↑	↑ ↑ ↑	□ □ □ □ □	4	8	SiCl ₄
P	↑↓	↑ ↑ ↑	□ □ □ □ □	3	8	PH ₃
P*	↑	↑ ↑ ↑	↑ □ □ □ □	5	10	PF ₅
S	↑↓	↑ ↓ ↑ ↑	□ □ □ □ □	2	8	H ₂ S
S*	↑↓	↑ ↑ ↑	↑ □ □ □ □	4	10	SF ₄
S**, Si ²⁻ , P ⁻	↑↓	↑ ↑ ↑	↑ □ □ □ □	6	12	SF ₆
Cl	↑	↑ ↑ ↑	↑ ↑ □ □ □	1	8	HCl
Cl*	↑↓	↑ ↓ ↑ ↓ ↑	□ □ □ □ □	3	10	ClF ₃
	↑↓	↑ ↓ ↑ ↑	↑ □ □ □ □			

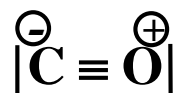
10.3 Dative Bonding

Bonding Electrons of a Covalent Bond can also be Contributed Exclusively by One Bonding Partner \Rightarrow Dative or Coordinative Bonding

Example



The **nominal charge** can be calculated by homogeneously distributing the bonding electrons to the bonding partners (homolysis)

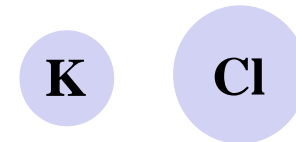


The real distribution of the bonding electron depends on the ability of the bonding partners to attract electrons (electron withdrawing character)

10.4 Atomic vs. Ionic Bond

In Chemical Compounds in most Cases no solely ionic nor atomic Bond exists!

KCl **K is weakly and Cl strongly electron withdrawing “ionic bond”**



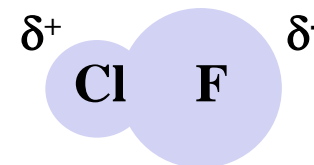
Cl₂ **Both partner are equally withdrawing**

“atomic bond”



Cl◀F **F is more withdrawing**

“polar atomic bond”



On what does the polarity of a covalent bond depend?

- 1. Anions (polarizability / size)**
- 2. Cations (charge density / ability to polarize anions)**

10.5 Dipoles and Dipole Moments

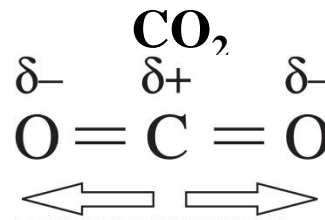
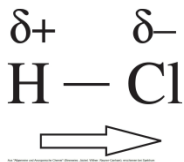
In Molecules with polar atomic Bonds partial electric Charges occur which might result in a Permanent Dipole Moment

Dipole moment

$$\mu = q \cdot d$$

with d = distance [m], q = charge [C]

HCl



Permanent dipole

non-permanent dipole

The observed dipole moment is a way to quantize the ionic character

(Linus Pauling)

Theoretical for H^+Cl^-

$$\mu = 1.60 \cdot 10^{-19} \text{ C} \cdot 127 \cdot 10^{-12} \text{ m} = 2.03 \cdot 10^{-29} \text{ Cm}$$

Experimentally found for HCl

$$\mu = 3.44 \cdot 10^{-30} \text{ Cm}$$

Ionic part of bonding: $3.44 \cdot 10^{-30} / 2.03 \cdot 10^{-29} \text{ Cm} * 100\% = 16.9\%$

10.6 Electronegativity

Electronegativity (X_E) of one Sort of Atoms or Ions describes the Ability to attract Electrons in a chemical Bond

Electronegativity (EN) is not experimentally measurable!

To determine EN values several formalisms were developed:

- 1. Pauling**
- 2. Allred and Rochow**
- 3. Mulliken**
- 4. Allen**

EN-values are tabulate in the periodic table!

The greater the difference in EN-values the more polar the atomic bond is or the more ionic character it exhibits

10.6 Electronegativity

Pauling Determines EN-Values from the Difference in Dissociation Energies, D , of the Homo-Nuclear to the corresponding Hetero-Nuclear Compounds

$$\Rightarrow D(AB) = \frac{1}{2} [D(A_2) + D(B_2)] + \Delta$$

Δ necessary, because a deviation from an arithmetical mean is contemplated!

Example: $D(H_2) = 435$ kJ/mol

$D(Cl_2) = 243$ kJ/mol

$D(HCl)_{\text{exp}} = 431$ kJ/mol

\Rightarrow arithmetical mean = 339 kJ/mol

$\Rightarrow \Delta = 92$ kJ/mol

The stabilizing contribution Δ is caused by bipolar arrangements A^+B^-

$$\Delta = 96 \cdot (\chi_H - \chi_{Cl})^2$$

$$\Rightarrow \chi_{Cl} = 3.2$$

Reference point necessary:

Highest value:

$$\chi_H = 2.2$$

$$\chi_F = 4.0$$

10.6 Electronegativity

Allred and Rochow determine EN-Values following an electrostatic Approach

Physical basics: Electronegativity, χ , is a way to quantize the Coulomb-force, F_c , acting on the valence electrons

$$\chi \sim F_c \sim Z^*/r^2$$

r = atomic radius, Z^* = effective atomic number
 $= OZ - \Sigma S_i$

S_i = Screening constant (according to Slater)

S_i = 0.0 for higher shells

0.35 for similar shells

0.85 for one shell lower (s- and p-electrons)

1.00 for one shell lower (d- and f-electrons)

1.00 for multiple shells lower (all electrons)

Adaption to Pauling-range:

$$\chi = 0.359 \sim Z^*/r^2 + 0.744$$

10.6 Electronegativity

EN-Values according to **Pauling** and **Allred and Rochow**

Electronegativity increases →

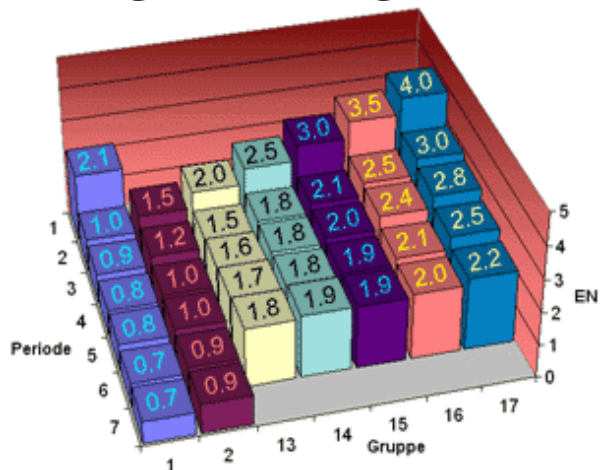
H 2.2 2.2																	He
Li 1.0 1.0	Be 1.5 1.5											B 2.0 2.0	C 2.5 2.5	N 3.0 3.1	O 3.4 3.5	F 4.0 4.1	Ne
Na 0.9 1.0	Mg 1.3 1.2											Al 1.6 1.5	Si 1.9 1.7	P 2.2 2.1	S 2.6 2.4	Cl 3.2 2.8	Ar
K 0.8 0.9	Ca 1.0 1.0	Sc 1.4 1.2	Ti 1.5 1.3	V 1.6 1.4	Cr 1.7 1.6	Mn 1.6 1.6	Fe 1.8 1.6	Co 1.9 1.7	Ni 1.9 1.8	Cu 1.9 1.8	Zn 1.7 1.7	Ga 1.8 1.8	Ge 2.0 2.0	As 2.2 2.2	Se 2.6 2.5	Br 3.0 2.7	Kr
Rb 0.8 0.9	Sr 1.0 1.0	Y 1.2 1.1	Zr 1.3 1.2	Nb 1.6 1.2	Mo 2.2 1.3	Tc 1.9 1.4	Ru 2.2 1.4	Rh 2.3 1.5	Pd 2.2 1.4	Ag 1.9 1.4	Cd 1.7 1.5	In 1.8 1.5	Sn 1.8 1.7	Sb 2.1 1.8	Te 2.1 2.0	I 2.7 2.2	Xe
Cs 0.8 0.9	Ba 0.9 1.0	La 1.1 1.1	Hf 1.3 1.2	Ta 1.5 1.3	W 2.4 1.4	Re 1.9 1.5	Os 2.2 1.5	Ir 2.2 1.5	Pt 2.3 1.4	Au 2.5 1.4	Hg 2.0 1.4	Tl 2.0 1.4	Pb 1.9 1.5	Bi 2.0 1.7			

Electronegativity
decreases ↓

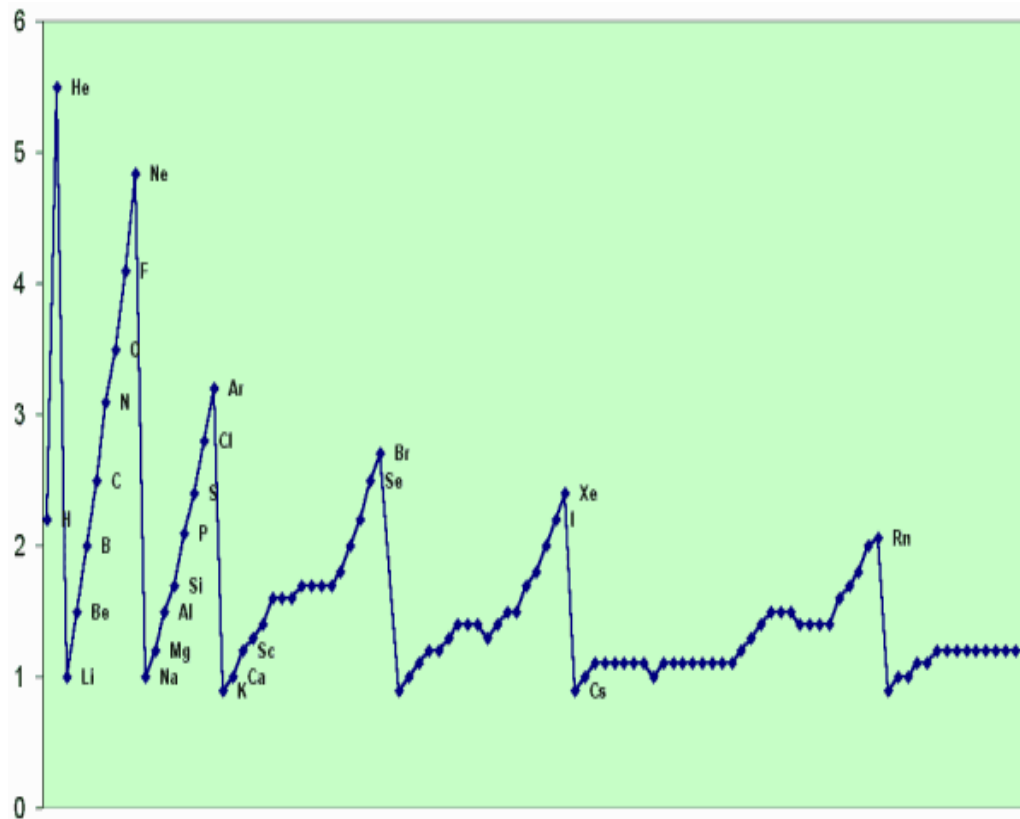
Noble metals exhibit a relatively high electronegativity according to Pauling!

10.6 Electronegativity

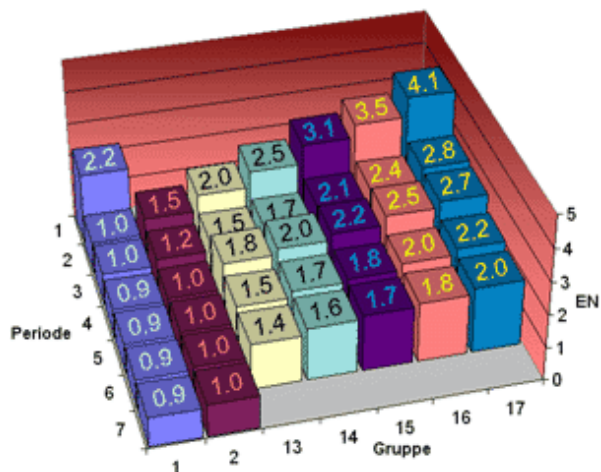
According to Pauling



Periodicity of EN according to Allred and Rochow



According to Allred and Rochow



Noble gases exhibit highest electronegativities according to Allred and Rochow !

10.6 Electronegativity

The Difference in EN Values of the binding Partners in particular chemical Bonds determines the bonding Type

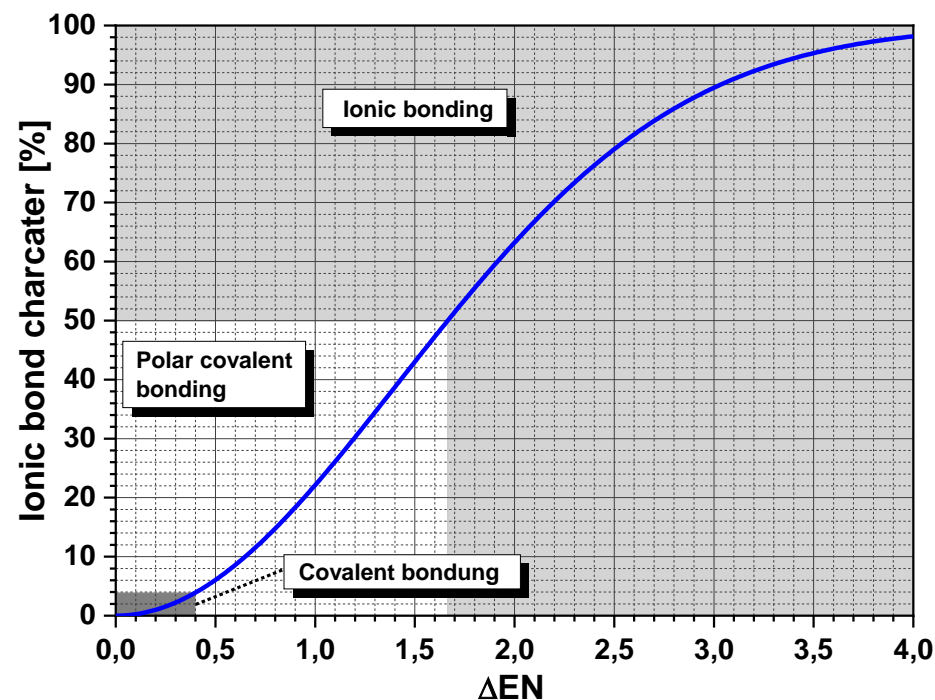
The greater the difference in the EN values (ΔEN), the more polar the atomic bond or the higher the ionic bond character P [%]

According to Pauling

$$P = \left(1 - e^{-0,25(EN_A - EN_B)^2} \right) \cdot 100\%$$

Results:

- **Covalent bonding** $\Delta EN < 0.4$
- **Polar covalent bonding** $0.4 < \Delta EN < 1.7$
- **Ionic bonding** $\Delta EN > 1.7$



10.7 Dipole-Dipole-Interactions

**The Interactions between Dipoles leads to Attraction of adjacent Molecules
(Dispersion Force or Van-der-Waals-Interaction)**

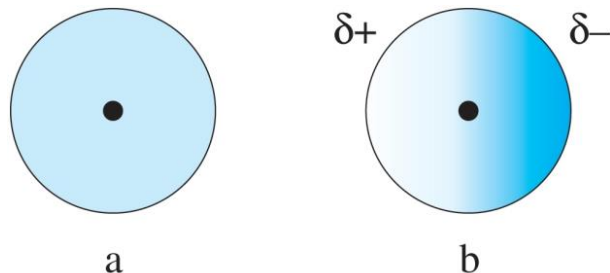
Temporary dipole

Noble gases

CH₄

SiH₄

GeH₄



weak intermolecular interactions

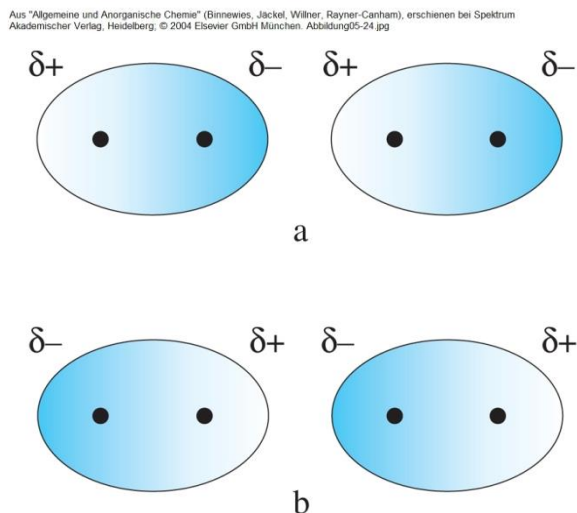
Permanent dipole

HF

HCl

HBr

HI



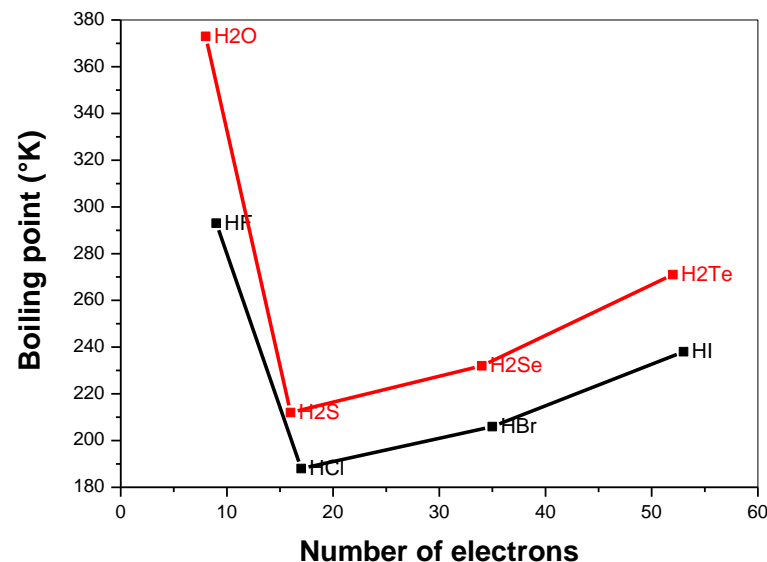
strong intermolecular interactions

10.8 Hydrogen Bonds

Hydrogen Bonds are the strongest intermolecular Interactions Occurring when Hydrogen is bound to a strongly electronegative Atom

Strength of X-H...X bonds

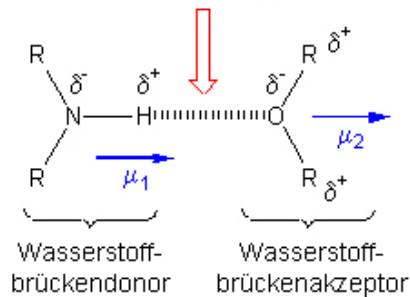
- 2 – 60 kJ/mol
- H-F > O-H > N-H



H₂O exhibits higher boiling point than
because every oxygen atom possesses two
free pairs of electrons
⇒ Anomaly of water!

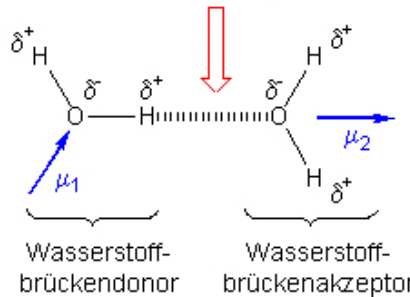
Fall 1 : 2 verschiedene Moleküle

Wasserstoffbrückenbindung



Fall 1 : 2 identische Moleküle

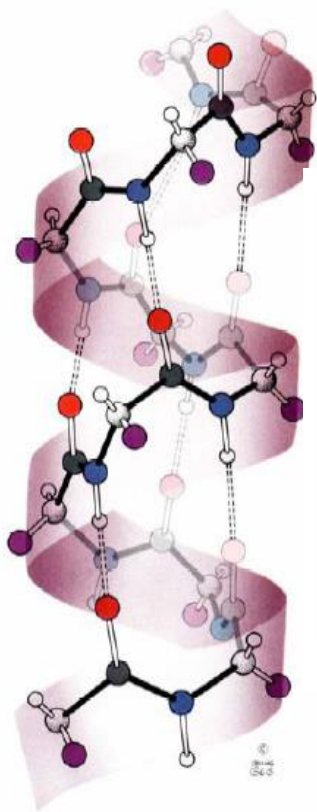
Wasserstoffbrückenbindung



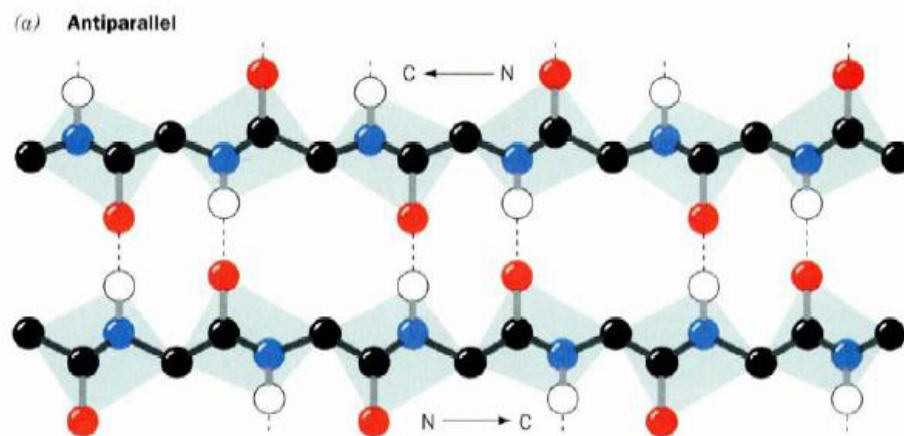
10.8 Hydrogen Bonds

Hydrogen Bonds are of fundamental Importance for Structures in Biology, e.g. for the spatial Arrangement of Proteins and DNA

α -helices in proteins

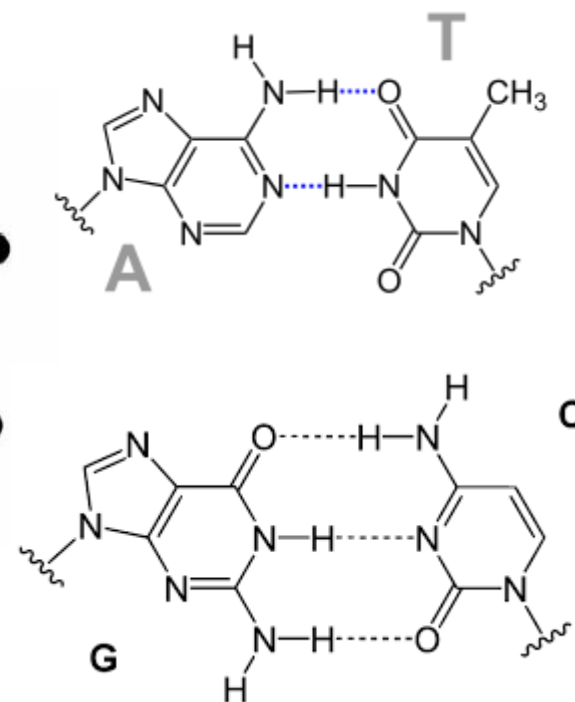


β -pleated sheets in proteins



Pairing of bases in DNA

A=T(2) oder G≡C (3)



10.9 Valence Bond Theory

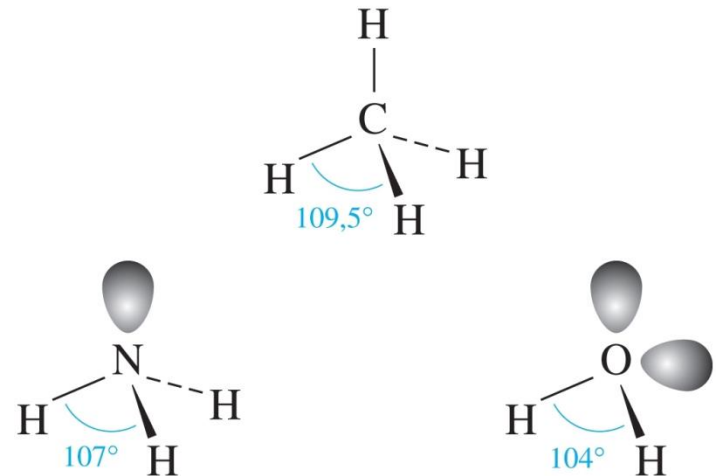
Chemical Bonds are based on the overlap of atomic Orbitals

Principals of VB-theory

1. Covalent bonds are based on the combination of unpaired electrons to pairs
2. The spins of the paired electrons must be anti-parallel
3. To form the maximum number of bonds it is assumed that prior to the formation of the bond, electrons are excited and occupy empty orbitals
4. The structure of the molecule is determined by the geometry of the orbitals of the central atom

But the actual molecular geometry cannot always be explained by only s-, p- and d-orbitals

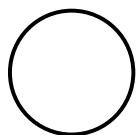
⇒ Hybridisation



10.9 Valence Bond Theory

Hybridisation describes the Formation of mixed (Hybrid) orbitals through Combination of Atomic Orbitals

s-Orbital + p-Orbital = sp, sp² or sp³-orbital

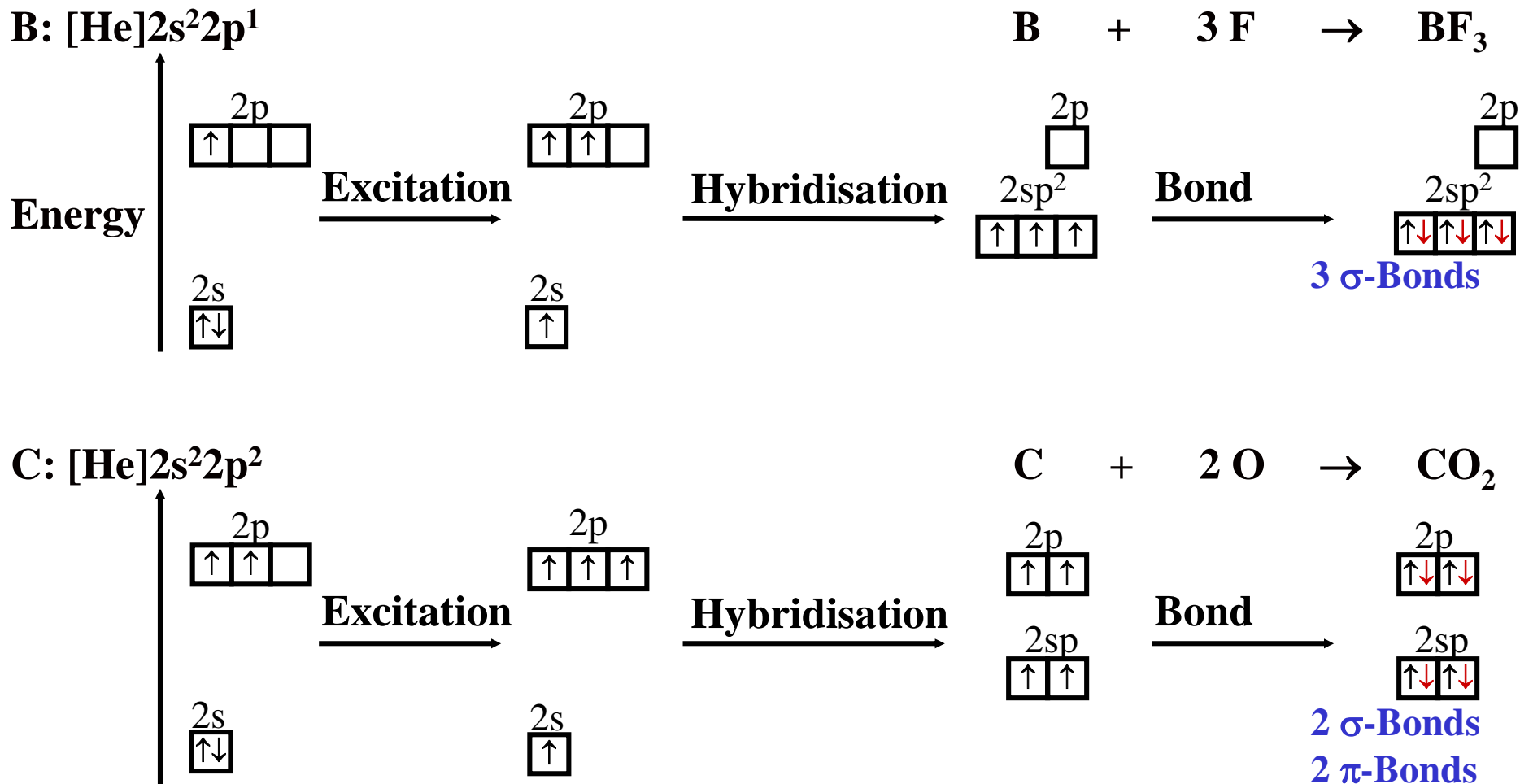


Hybrid orbitals overlap better and thus lead to more stable bonds

No. of participating orbitals			Kind of hybridisation	No. of hybrid orbital	Arrangement of the orbitals	Example
s	p	d				
1	1	0	sp	2	linear	BeF ₂
1	2	0	sp ²	3	trigonal-planar	BF ₃
1	3	0	sp ³	4	tetrahedral	CF ₄
1	3	1	sp ³ d	5	trigonal-bipyramidal	PF ₅
1	3	2	sp ³ d ²	6	octahedral	SF ₆
1	3	3	sp ³ d ³	7	pentagonal-bipyramidal	IF ₇

10.9 Valence Bond Theory

Hybridisation and Bonding Situation in BF_3 and CO_2



10.10 Molecular Orbital Theory

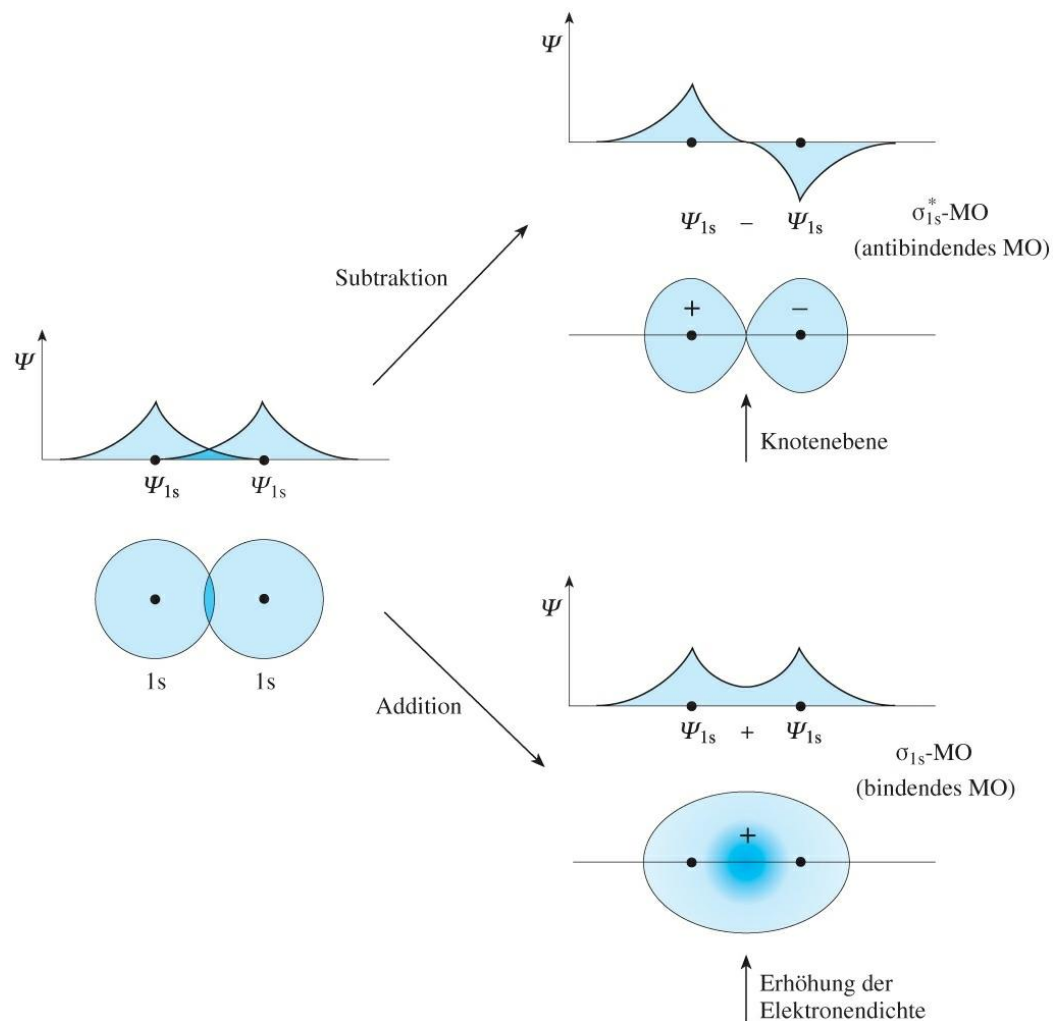
Molecular Orbitals (MOs) are formed by Linear Combination, i.e. Summation or Subtraction, of Atomic Orbitals according to $\psi = \psi_1 + \psi_2$ and $\psi = \psi_1 - \psi_2$

Some remarks about MOs

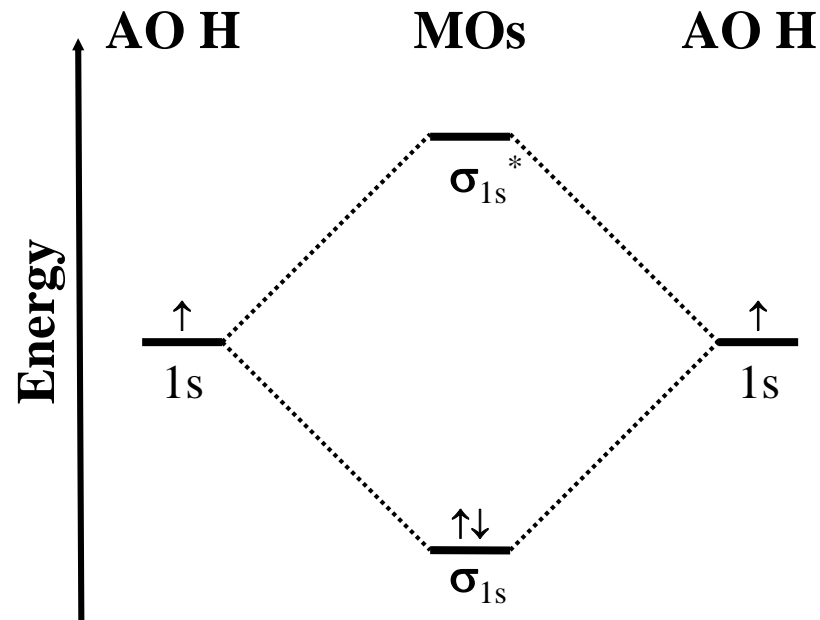
1. Atomic orbitals (AOs) can only overlap, if the wave functions have the same algebraic sign in the relevant range
2. From two AOs two MOs are formed, one bonding and one anti-bonding MO
3. A significant overlap requires similar energy of the AOs
4. Every MO contain a maximum of two electrons with a spin of $+1/2$ and $-1/2$
5. The electronic configuration of a molecule is given, analogous to atoms, by the occupation of the MOs in order of increasing energy
6. The bonding order (B.O.) is half the difference of the number of bonding minus the number of anti-bonding electrons

10.10 Molecular Orbital Theory

Formation of MOs in the H₂ Molecule



Energy level diagram of H₂ (Molecular orbital diagram)



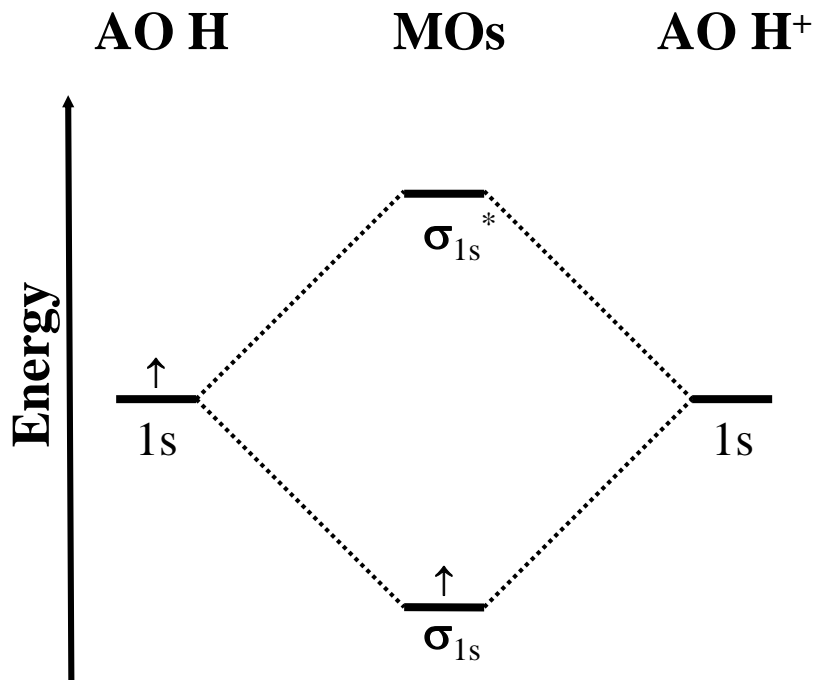
(Energy levels are depicted as dashes)

$$\text{B.O.}(\text{H}_2) = 1$$

10.10 Molecular Orbital Theory

Bonding Order in H_2^+ and He_2^+

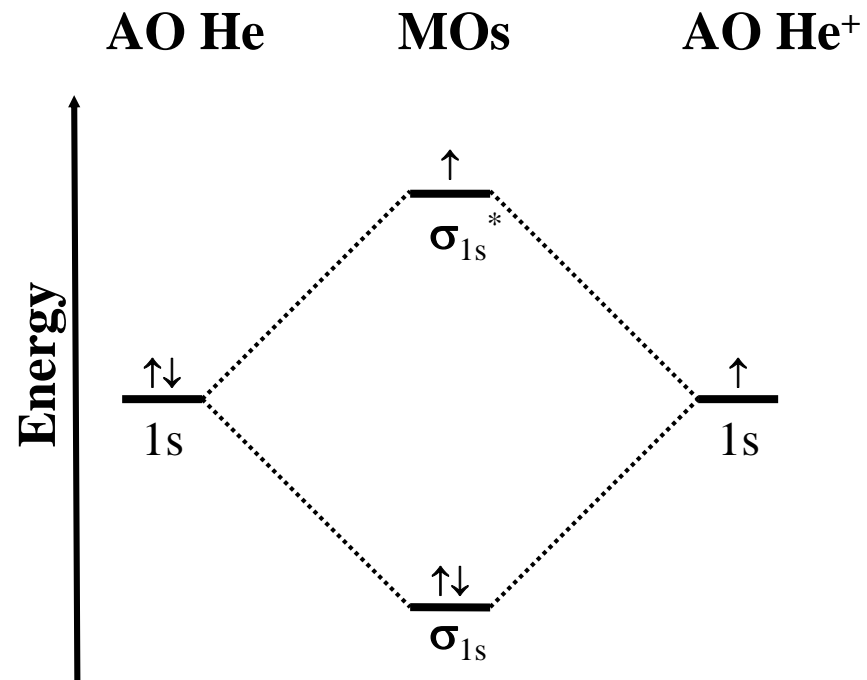
Molecular orbital diagram of H_2^+



$$\text{B.O.} = 0.5 * (1 - 0) = 0.5$$

$\Rightarrow \text{H}_2^+$, HeH^+ and He_2^+ are stable molecules, He_2 is not (Lit.: Nature 568 (2019) 357)

Molecular orbital diagram of He_2^+

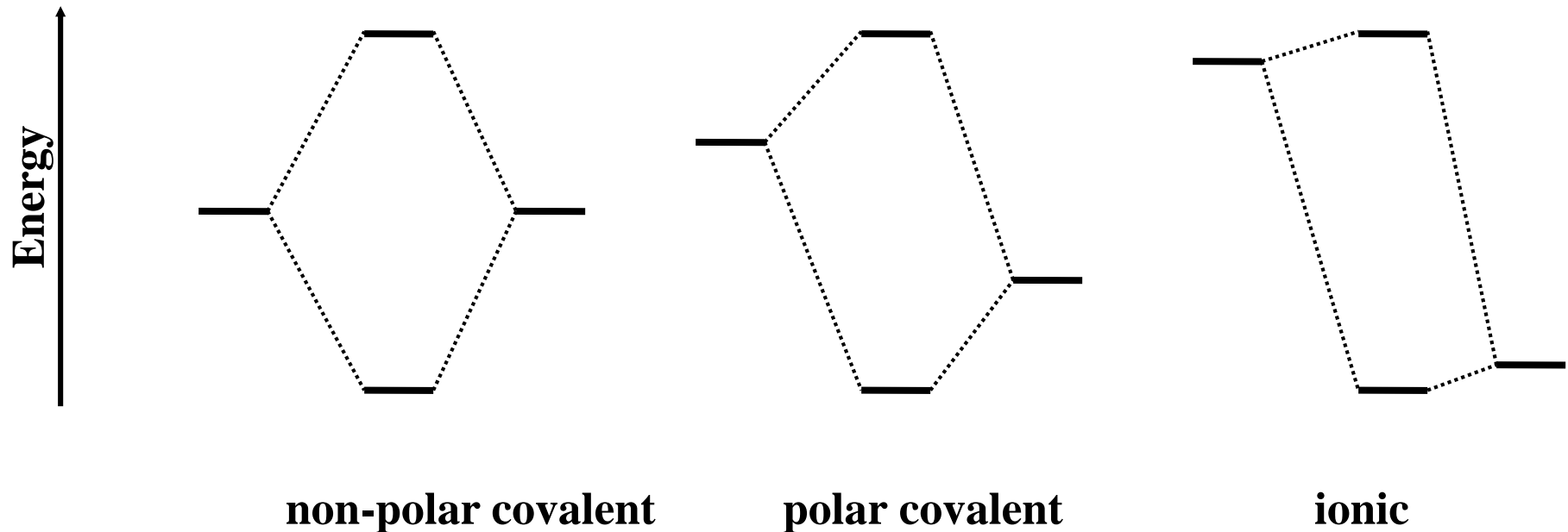


$$\text{B.O.} = 0.5 * (2 - 1) = 0.5$$

10.10 Molecular Orbital Theory

Stability of Covalent Bonds According to MO-Theory

- Energy-criterion: the more similar energies of two AO's the greater the resulting energy win of the binding MO**

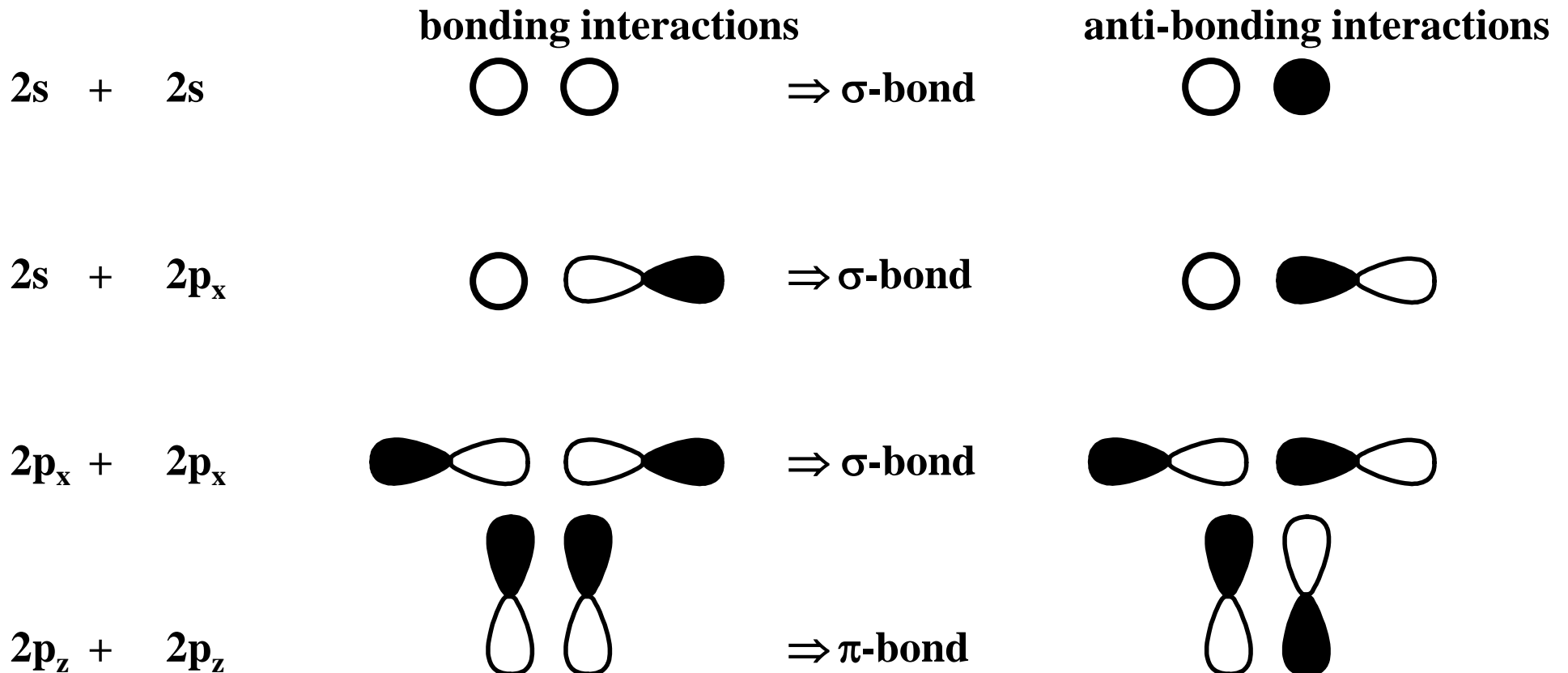


- Overlap criterion: for a stable bond the interacting AO's must overlap sufficiently**

10.10 Molecular Orbital Theory

Stability of Covalent Bonds According to MO-Theory

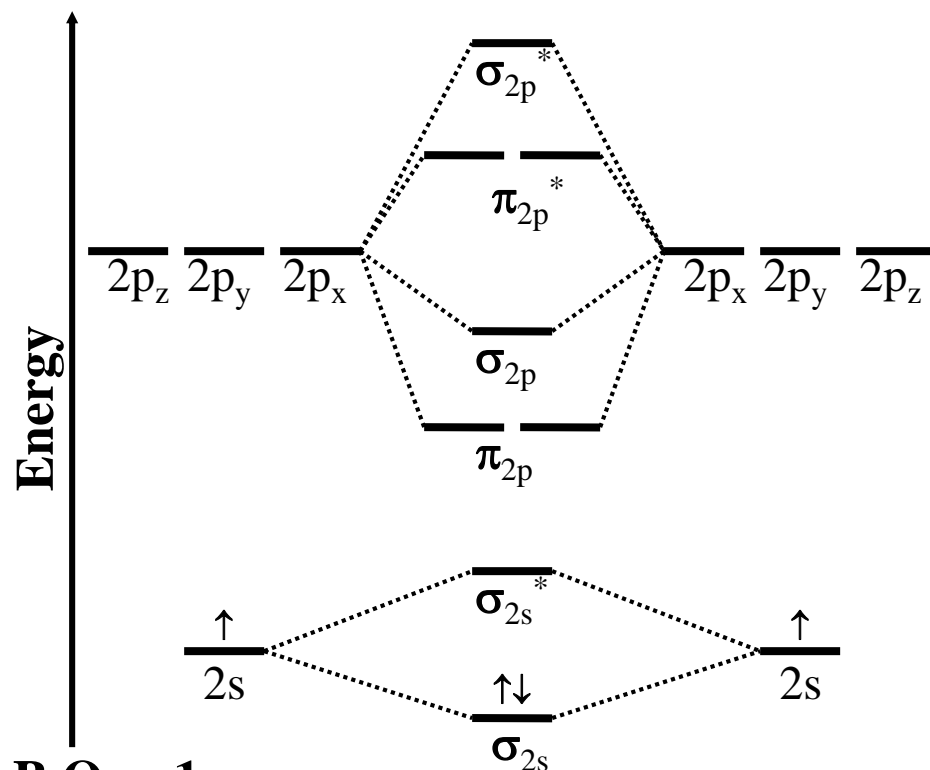
3. **Symmetry-criterion:** For a stable bond the interacting AOs must fit in symmetry



10.10 Molecular Orbital Theory

MO-Diagrams of homonuclear diatomic Molecules (Energetic Order of MOs by Ultraviolet-Photoelectron-Spectroscopy)

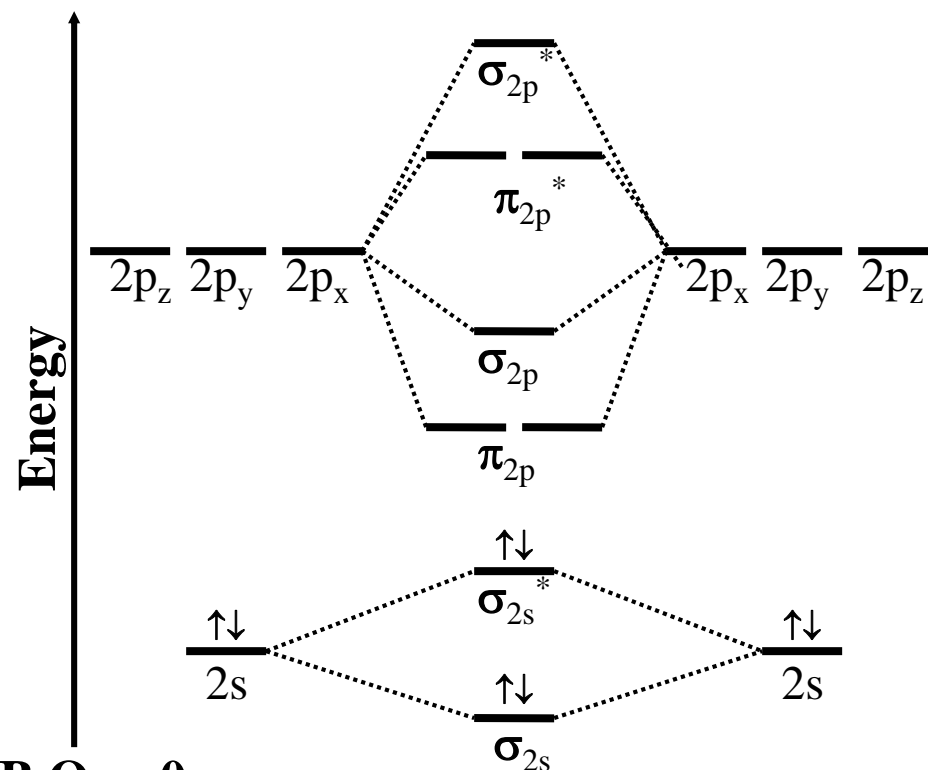
Li₂



B.O. = 1

Li₂ exists in gaseous phase

Be₂

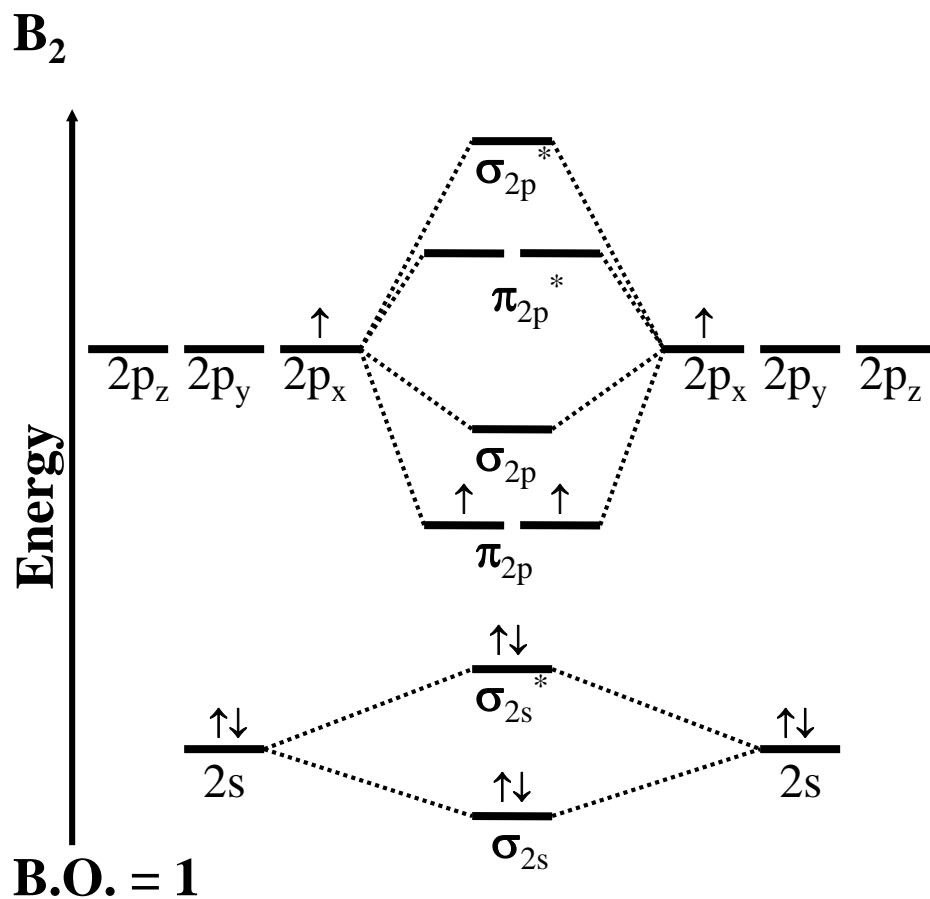


B.O. = 0

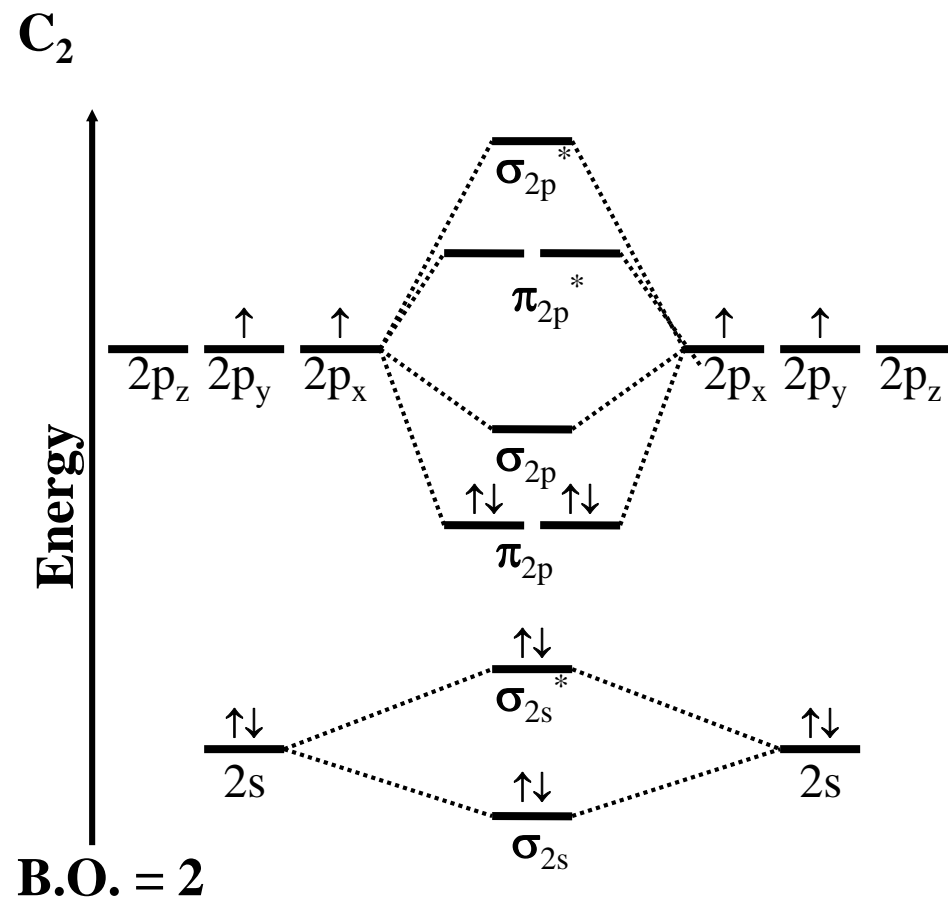
Be₂ is unstable

10.10 Molecular Orbital Theory

MO-Diagrams of homonuclear diatomic Molecules



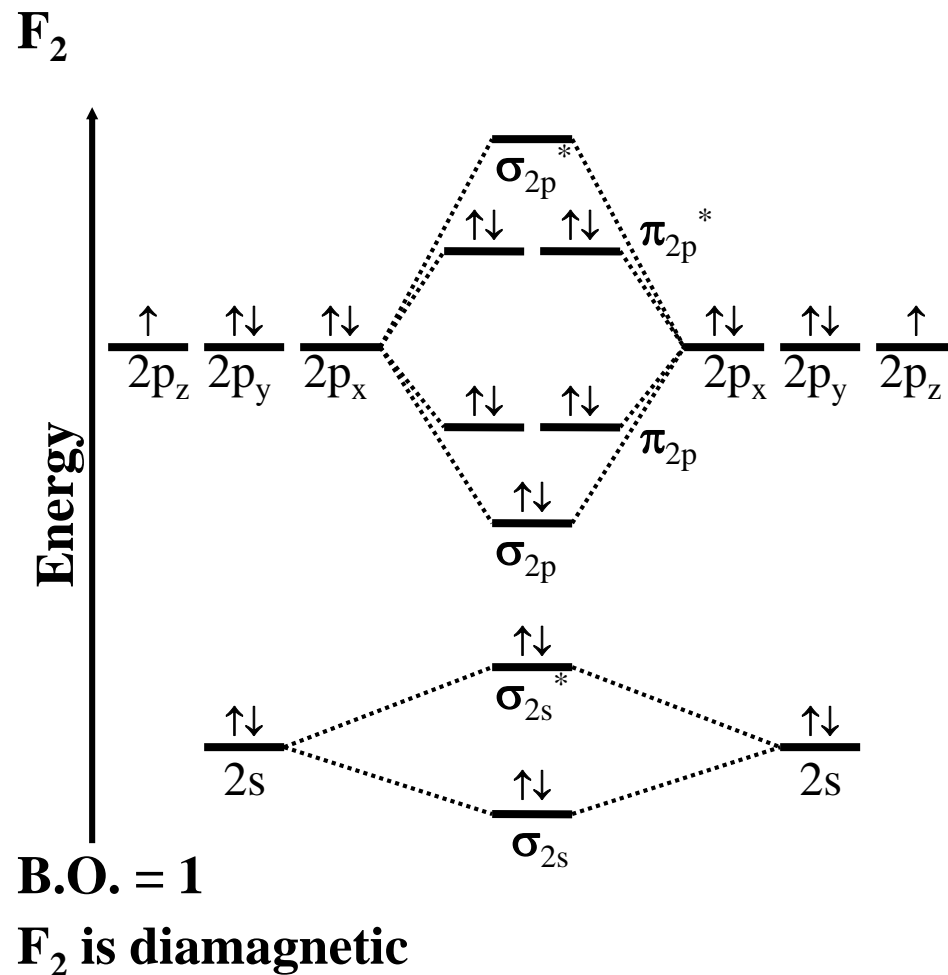
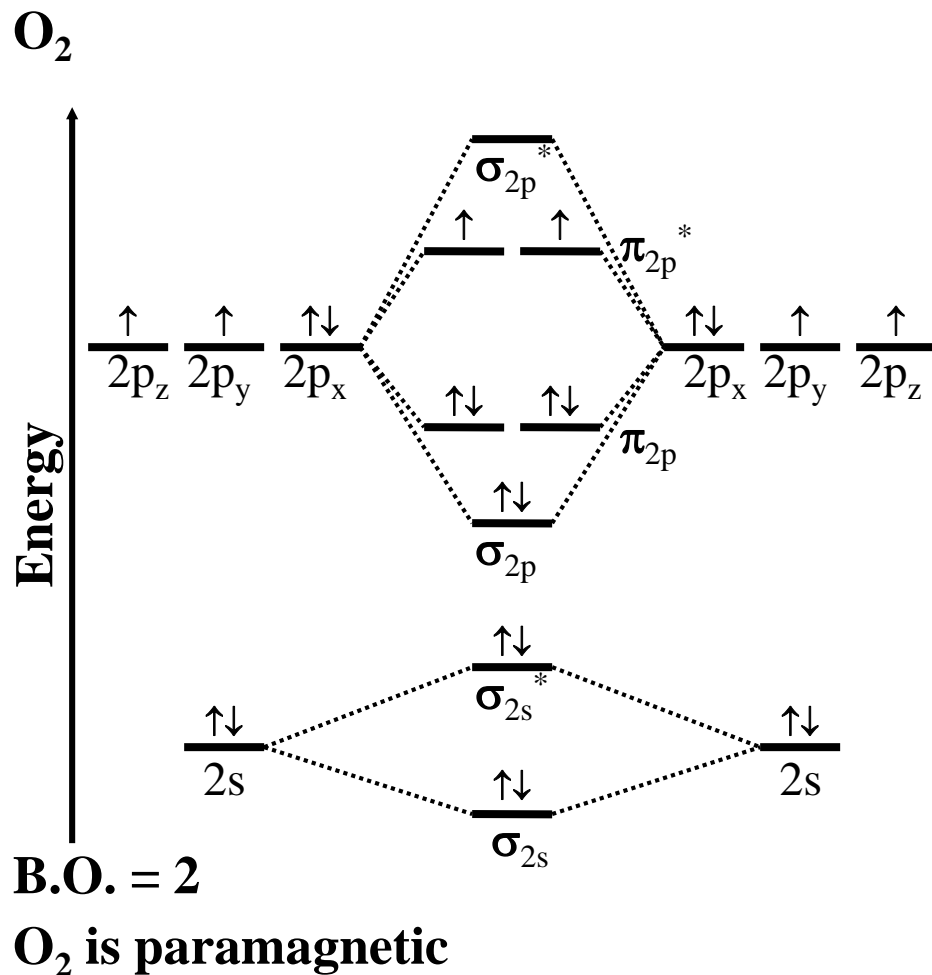
B₂ exists in gaseous phase



C₂ exists in gaseous phase

10.10 Molecular Orbital Theory

MO-Diagrams of homonuclear diatomic Molecules



10.10 Molecular Orbital Theory

Bonding Properties of homonuclear diatomic Molecules

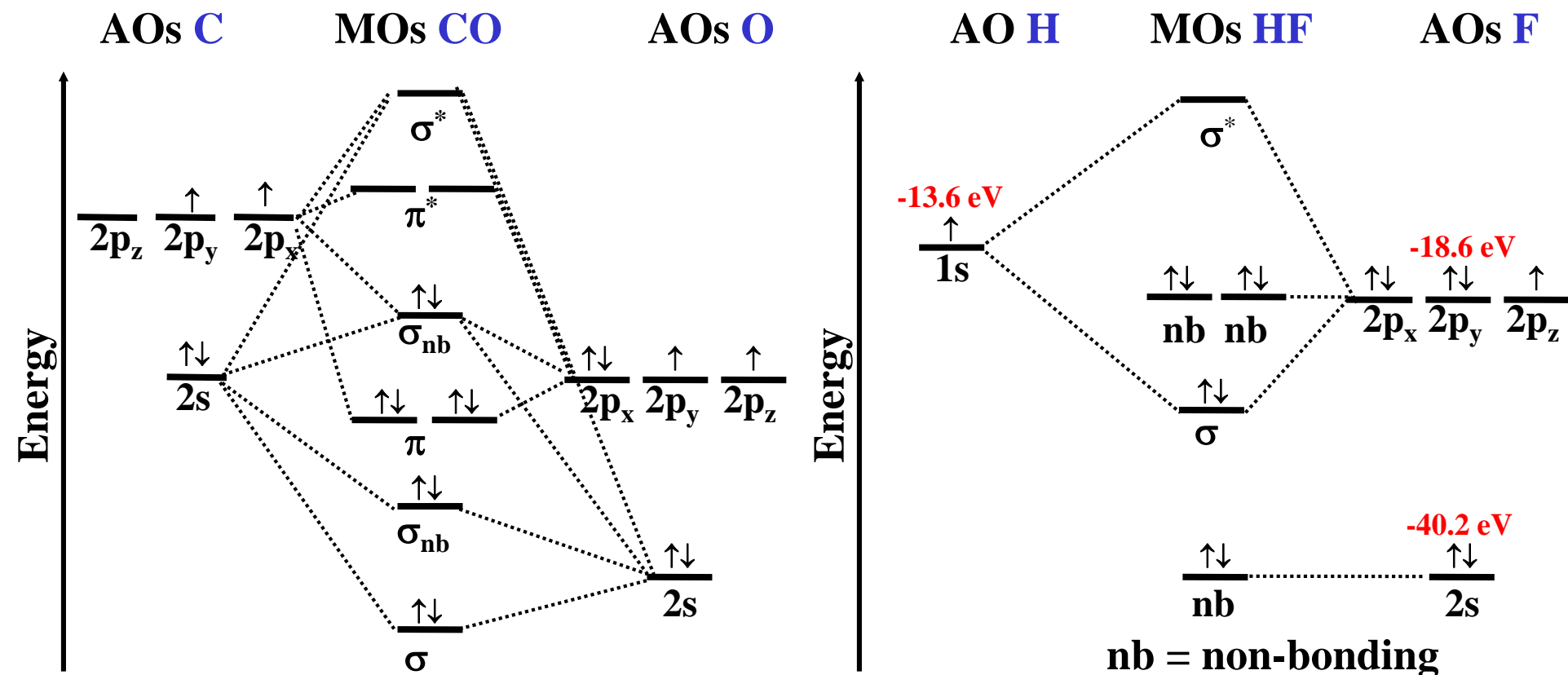
Molecule or ion	Number of valence electrons	Bonding order	Dissociation energy [kJ/mol]	Distance of nuclei [pm]
H_2^+	1	0.5	256	106
H_2	2	1	432	74
He_2^+	3	0.5	~300	108
He_2	4	0	0	-
Li_2	2	1	105	267
Be_2	4	0	0	-
B_2	6	1	289	159
C_2	8	2	628	131
N_2	10	3	942	109
O_2	12	2	494	121
F_2	14	1	151	142
Ne_2	16	0	0	-

⇒ Ionised (or excited) noble gas atoms can form compounds!

10.10 Molecular Orbital Theory

MO-Diagrams of heteronuclear diatomic Molecules

- ⇒ The energy of the AOs of the two bonding partners is different in most cases
- ⇒ Energy of the AOs is determined by photo electron spectroscopy (UPS)



10.11 Nomenclature of Binary Molecular Compounds

Name of Molecule = Name of the More electropositive Element + Name of the more electronegative Element

More electropositive element

English name: Nitrogen, oxygen, phosphorus, sulphur, arsenic, selenium, antimony, ...

More electronegative element

Latin name, with the suffix replaced by -ide:

carbide, silicide, germanide, nitride, phosphide, arsenide, oxide, sulphide, selenide ...

<u>Example</u>	<u>Name</u>	<u>Prefix</u>	<u>Number</u>
N_2O	Dinitrogen oxide	mono-	1
NO	Nitrogen monoxide	di-	2
N_2O_3	Dinitrogen trioxide	tri-	3
NO_2	Nitrogen dioxide	tetra-	4
N_2O_4	Dinitrogen tetraoxide	penta-	5
N_2O_5	Dinitrogen pentoxide	hexa-	6

But: there is a number of unsystematic names: water, ammonia, hydrazine etc.

11. Metal Bond

Contents

11.1 Properties of Metals

11.2 Crystal Structures of Metals

11.3 Radii of Metal Atomes

11.4 Metallic Bond

11.5 Conductor, Intrinsic Semi-Conductor, Insulator

11.6 Doped Semi-Conductors

11.7 Comparison of Bonding Types



*Atomium in Brussels, 1958
(Fe-unit cell magnified by a
factor of $165 \cdot 10^{12}$)*

11.1 Properties of Metals

80% of all known Elements are Metals and exhibit a Number of similar Features

Typical Properties

- **Low ionisation energies (< 10 eV) or electropositive character, i.e. metals easily form cations**
- **Metallic gloss on surface**
- **Elasticity and plastic deformability**
- **Good thermal and electric conductivity that decreases with increasing temperature**
- **Metallic properties are preserved in the melt and are lost only in the vapour phase**

⇒ Metallic properties are thus linked to the existence to bigger atomic unions

11.1 Properties of Metals

The electrical Conductivity depends strongly on the electronic Configuration

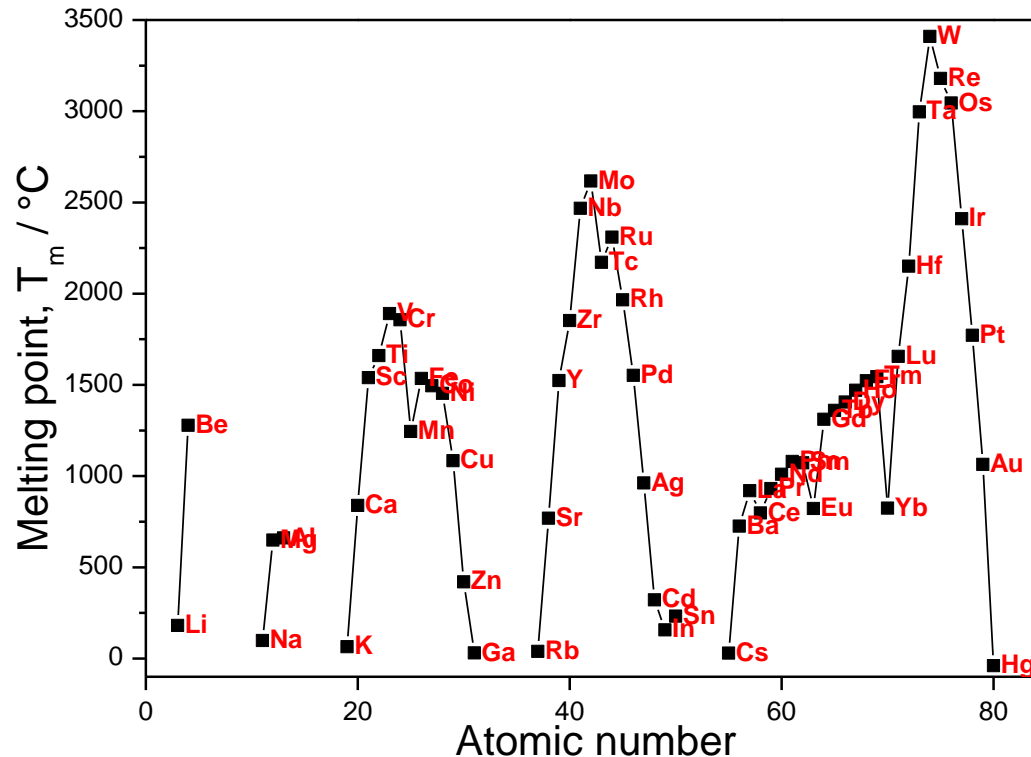
Li 11.8	Be 18														
Na 23	Mg 25											Al 40			
K 15.9	Ca 23	Sc	Ti 1.2	V 0.6	Cr 6.5	Mn 20	Fe 11.2	Co 16	Ni 16	Cu 65	Zn 18	Ga 2.2			
Rb 8.6	Sr 3.3	Y	Zr 2.4	Nb 4.4	Mo 23	Tc	Ru 8.5	Rh 22	Pd 10	Ag 66	Cd 15	In 12	Sn 10	Sb 2.8	
Cs 5.6	Ba 1.7	La 1.7	Hf 3.4	Ta 7.2	W 20	Re 5.3	Os 11	Ir 20	Pt 10	Au 49	Hg 4.4	Tl 7.1	Pb 5.2	Bi 1	

Electrical conductivity of metals at 0 °C in $10^6 \Omega^{-1}\text{m}^{-1}$

The highest electrical conductivities exhibit the elements of the 1. sub group (group 11) with the electronic configuration $[\text{Ar}]3d^{10}4s^1$, $[\text{Kr}]4d^{10}5s^1$, $[\text{Xe}]5d^{10}6s^1$

11.1 Properties of Metals

All Metals, with Exception of Mercury, are Solids at Room Temperature



- Metals with the lowest melting points are: Hg ($-39\text{ }^{\circ}\text{C}$), Cs ($29\text{ }^{\circ}\text{C}$), Ga ($30\text{ }^{\circ}\text{C}$), and Rb ($39\text{ }^{\circ}\text{C}$)
- The highest melting point appear for the valence electron-rich transition metals (e.g. Ti, V, Cr, Nb, Mo, Ru, Ta, W, Re)

11.1 Properties of Metals

Main Group Elements have one or a Maximum of two Oxidation States, Transition Metals on the other Hand may possess a large Number of Oxidation States

Manganese: $Mn^0 \rightarrow [Mn(H_2O)_4]SO_4 \rightarrow MnO(OH) \rightarrow MnO_2 \rightarrow MnO_4^{3-} \rightarrow MnO_4^{2-} \rightarrow MnO_4^-$

s^1	s^2	s^2p^1	s^2p^2	s^2p^3
Li +1	Be +2			
Na +1	Mg +2	Al +3		
K +1	Ca +2	Ga +3		
Rb +1	Sr +2	In +1 +3	Sn +2 +4	Sb +3 +5
Cs +1	Ba +2	Tl +1 +3	Pb +2 +4	Bi +3 +5

Sc $3d^14s^2$	Ti $3d^24s^2$	V $3d^34s^2$	Cr $3d^54s^1$	Mn $3d^54s^2$	Fe $3d^64s^2$	Co $3d^74s^2$	Ni $3d^84s^2$	Cu $3d^{10}4s^1$	Zn $3d^{10}4s^2$
+3	+2 +3 +4	+2 +3 +4 +5	+2 +3 +6	+2 +3 +4 +7	+2 +3	+2 +3	+2	+1 +2	+2
Sc_2O_3	TiO Ti_2O_3 TiO ₂	V_2O_3 VO ₂ V_2O_5	Cr_2O_3	Mn_2O_3 MnO ₂ Mn_2O_6 Mn ₂ O ₇	FeO Fe_2O_3	CoO Co ₂ O ₃	NiO	Cu ₂ O CuO	ZnO

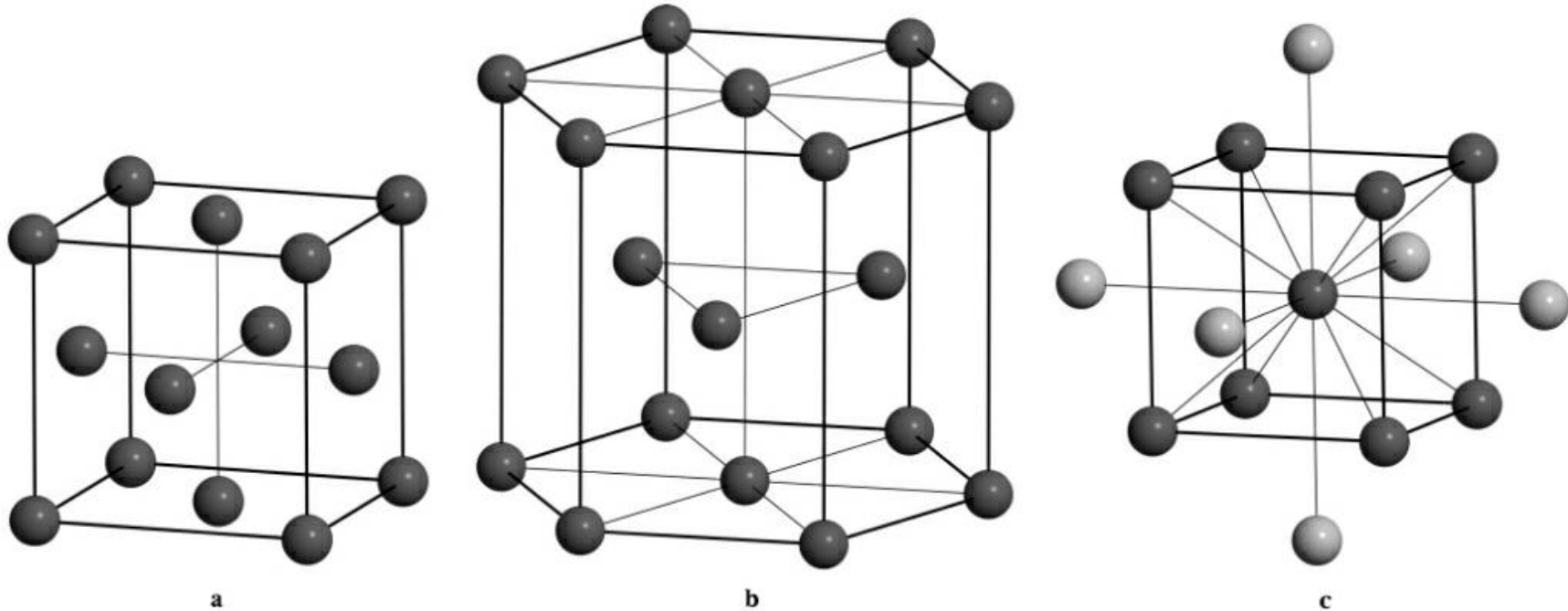
↓
↓
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→ **“ s^2 -Ions“**
⇒ *reactive*

→ **“redox-labile or reactive ions“**
⇒ *metalloenzymes (transport of electrons)*
⇒ *catalysts (redox processes)*

11.2 Crystal Structure of Metals

80% of the metallic Elements crystallise in an A_1 -, A_2 - or A_3 -Kind of Structure



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung06-08.jpg

A_1 -Type

Cubic-dense

Coordination number 12

Cu, Ag, Au, Ni, Pd, Pt, Rh, ...

A_3 -Type

Hexagonal-dense

Coordination number 12

Be, Mg, Y, La, Ti, Zr, ...

A_2 -Type

Cubic-body centred

Coordination number 8

Li, Na, K, Rb, Cs, Ba, ...

11.3 Radii of Metal Atoms

**Atomic Radii of the Metals can easily be calculated from their Crystal Structures
(Radius = Half of interatomic Distance)**

Li 156	Be 112	Radii for coordination number 12 in pm											Al 143	
Na 237	Mg 160												K 237	Ca 197
Rb 252	Sr 215	Y 181	Zr 160	Nb 146	Mo 139	Tc 135	Ru 134	Rh 134	Pd 137	Ag 144	Cd 152	In 166	Sn 158	
Cs 268	Ba 223	La 187	Hf 158	Ta 146	W 140	Re 137	Os 135	Ir 135	Pt 138	Au 144	Hg 155	Tl 171	Pb 174	Bi 182

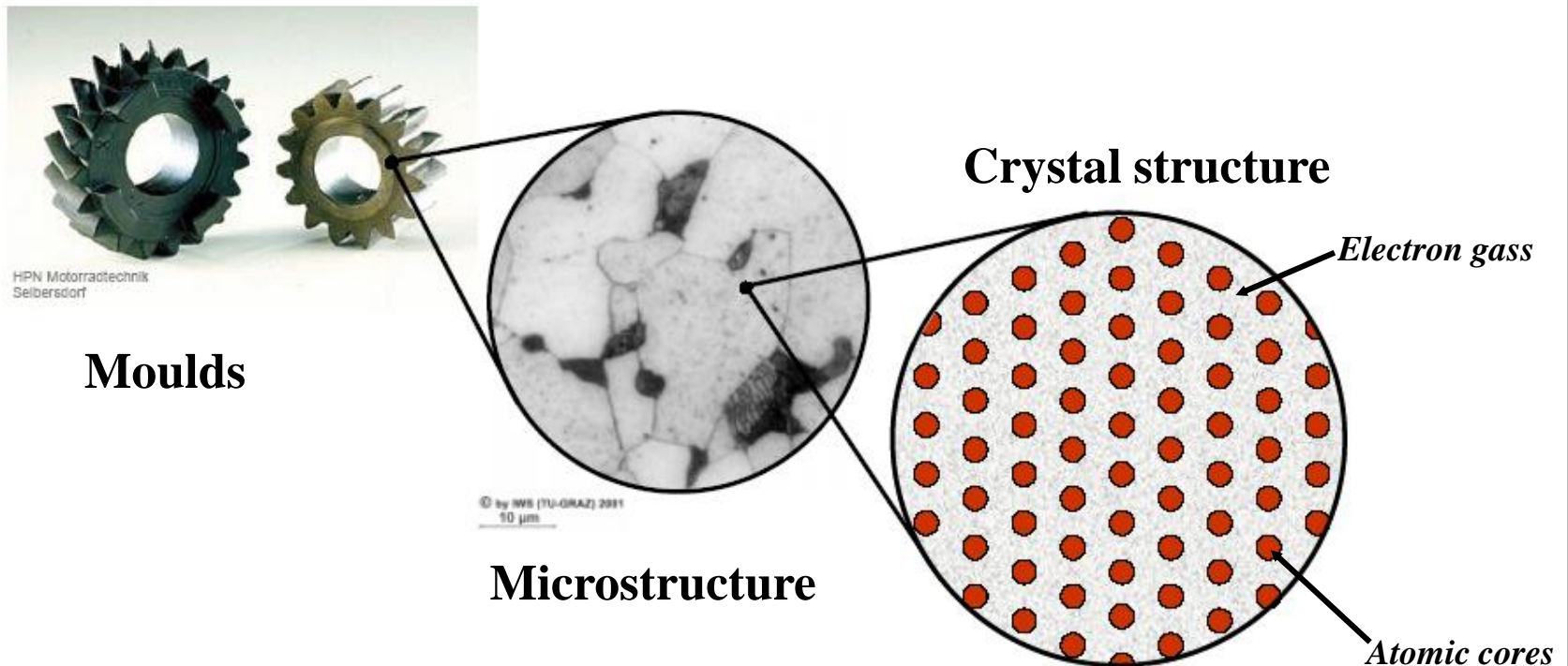
CN	Radius
12	1.00
8	0.97
6	0.96
4	0.88

- The atomic radii range from 110 and 270 pm
- The atomic radius is a periodic feature in the periodic table
- The radii of the 4d- and 5d-metals (5. and 6. period) are comparable due to the lanthanide contraction

11.4 Metallic Bond

Electron-Gas-Model

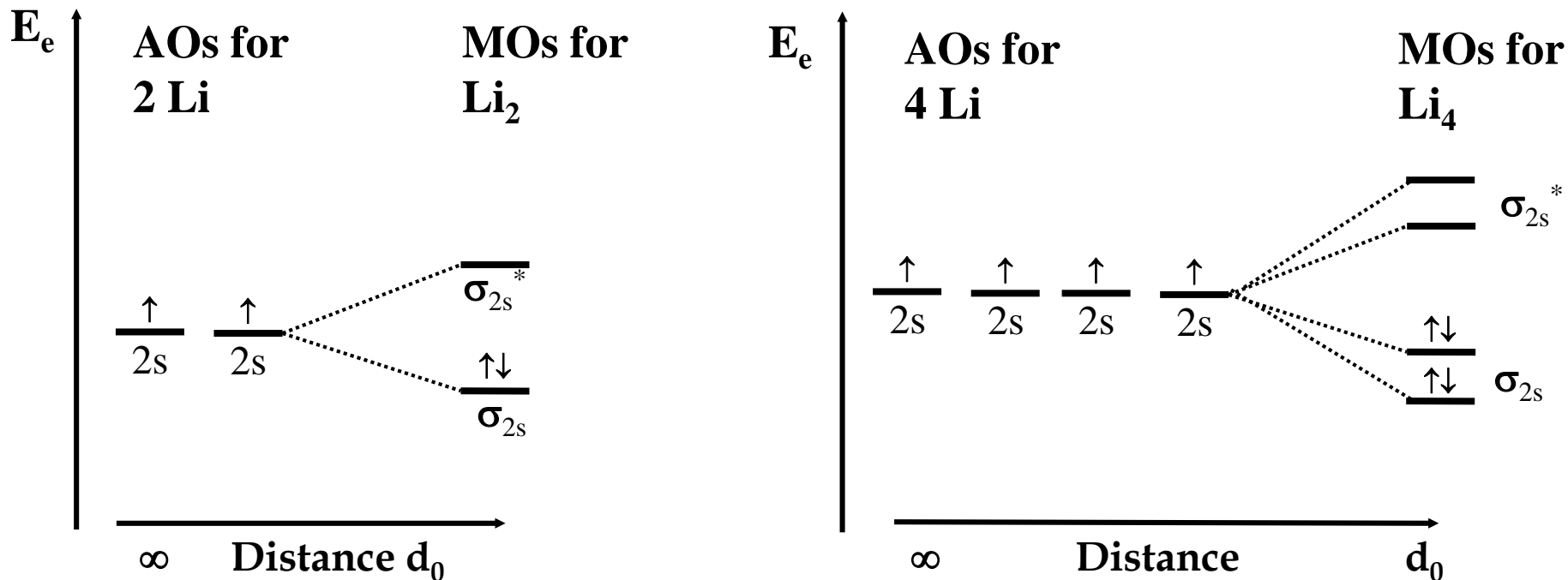
Metals consist of small crystals (crystallites). The atomic cores are arranged periodically and the valence electrons form an “electron gas”



The model explains the high electrical and thermal conductivity but not the thermodynamic (thermal capacity) or the optical properties

11.4 Metallic Bond

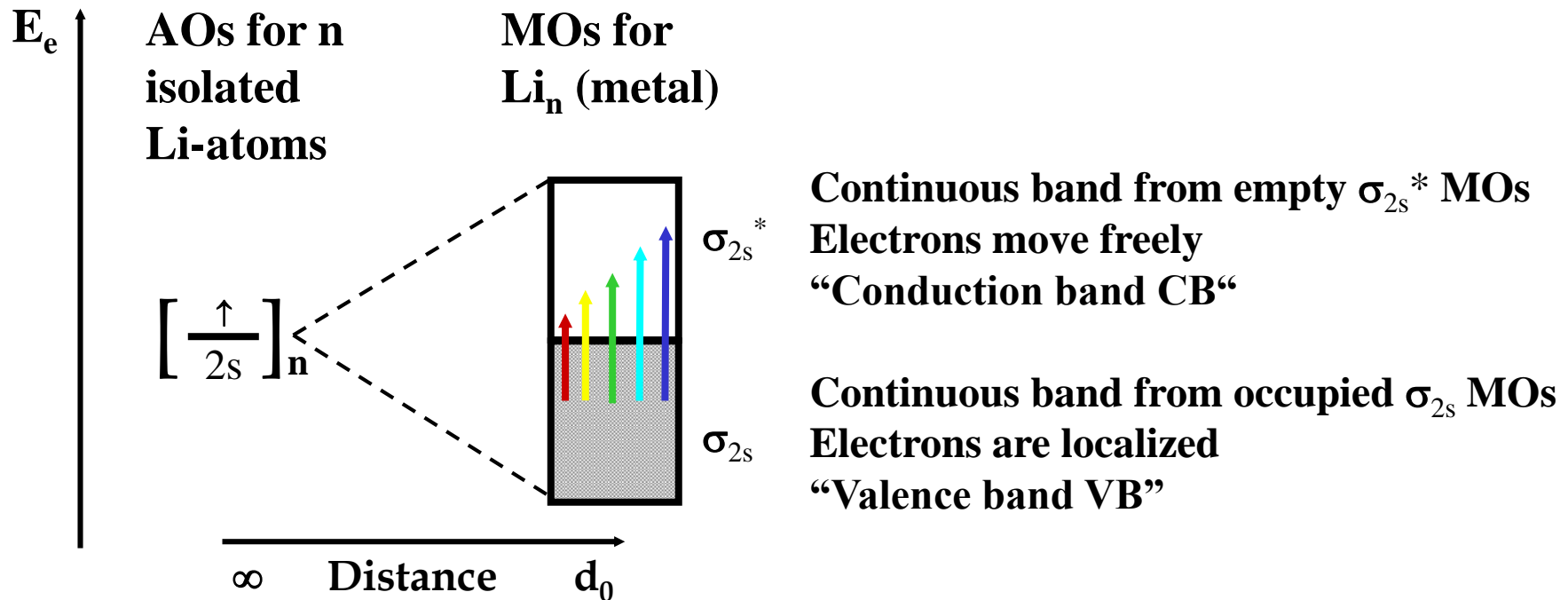
Model of Energetic Bands



n Li atoms possess n $2s$ AOs and thus form $n/2$ bonding σ_{2s} and $n/2$ Anti-bonding σ_{2s}^* MOs

11.4 Metallic Bond

Model of Energetic Bands

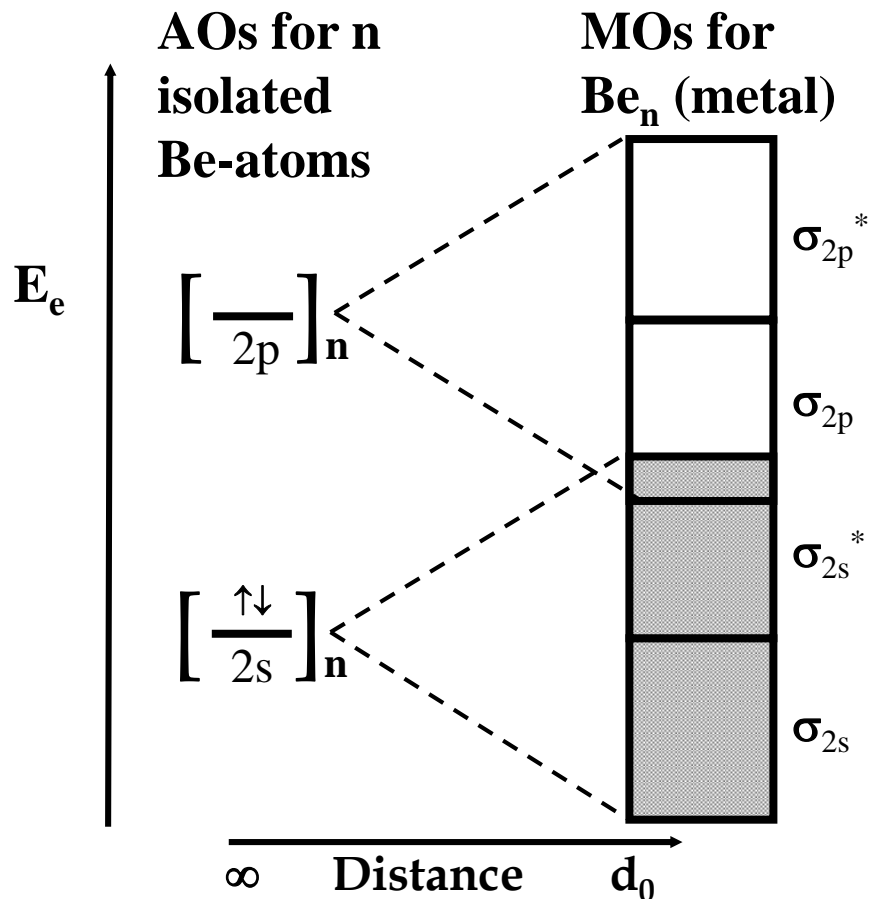


Electrons from the valence band can be promoted into the conduction band even by the smallest excitation energies \Rightarrow Absorption and emission of all wavelengths without loss of energy

\Rightarrow Broad reflection (mirror) and metallic glare (polished metallic surfaces)

11.4 Metallic Bond

Model of Energetic Bands

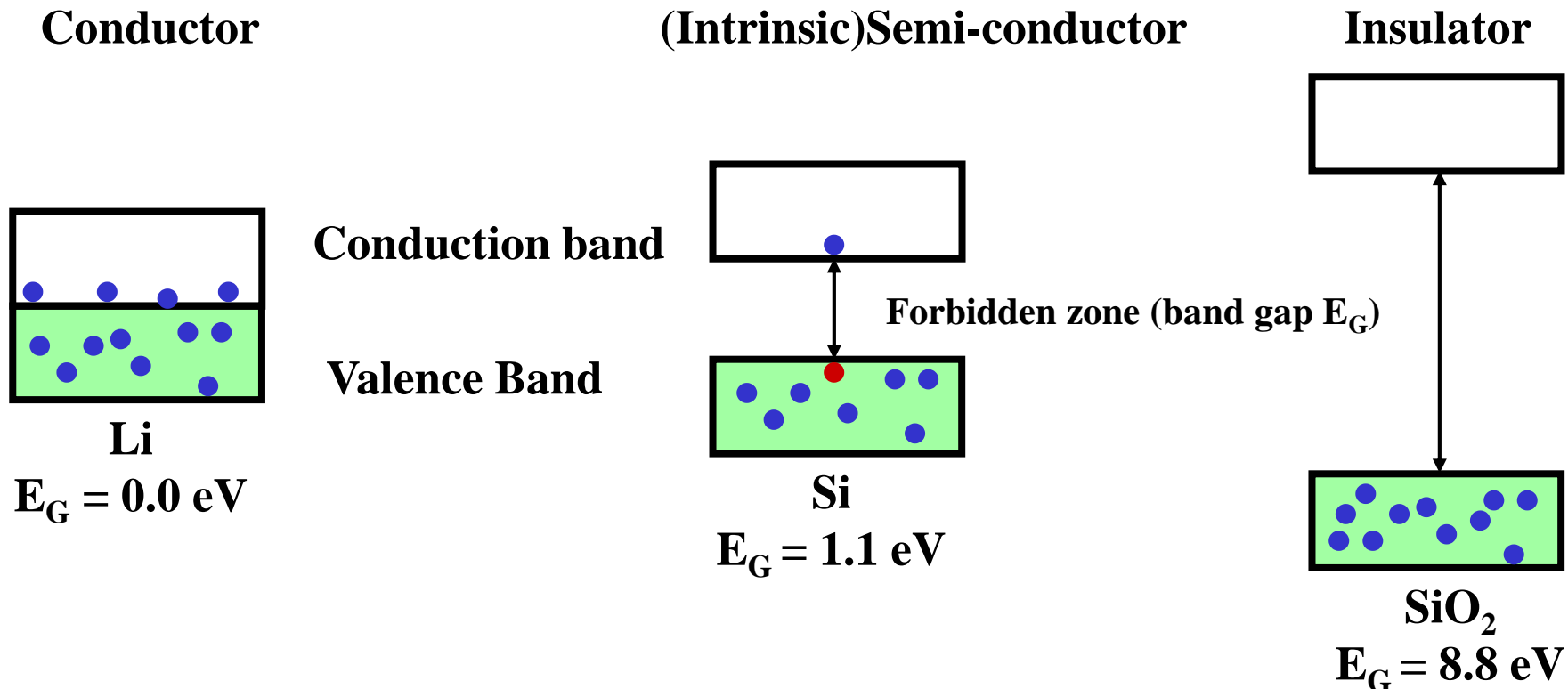


→ Overlap of occupied σ_{2s}^* band and the empty σ_{2p} band

Electrons from the fully occupied σ_{2s}^* band are promoted into the empty σ_{2p} band creating conductivity

11.5 Conductor, Intrinsic Semi-Conductor, Insulator

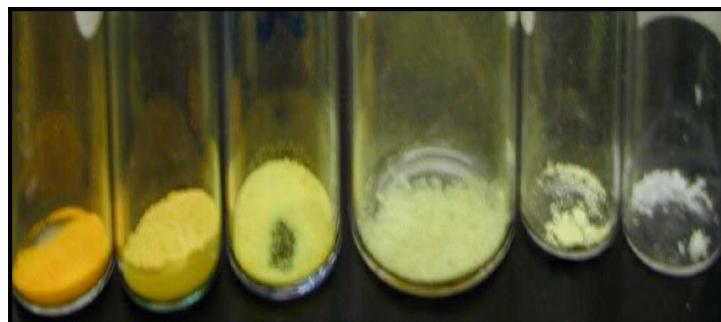
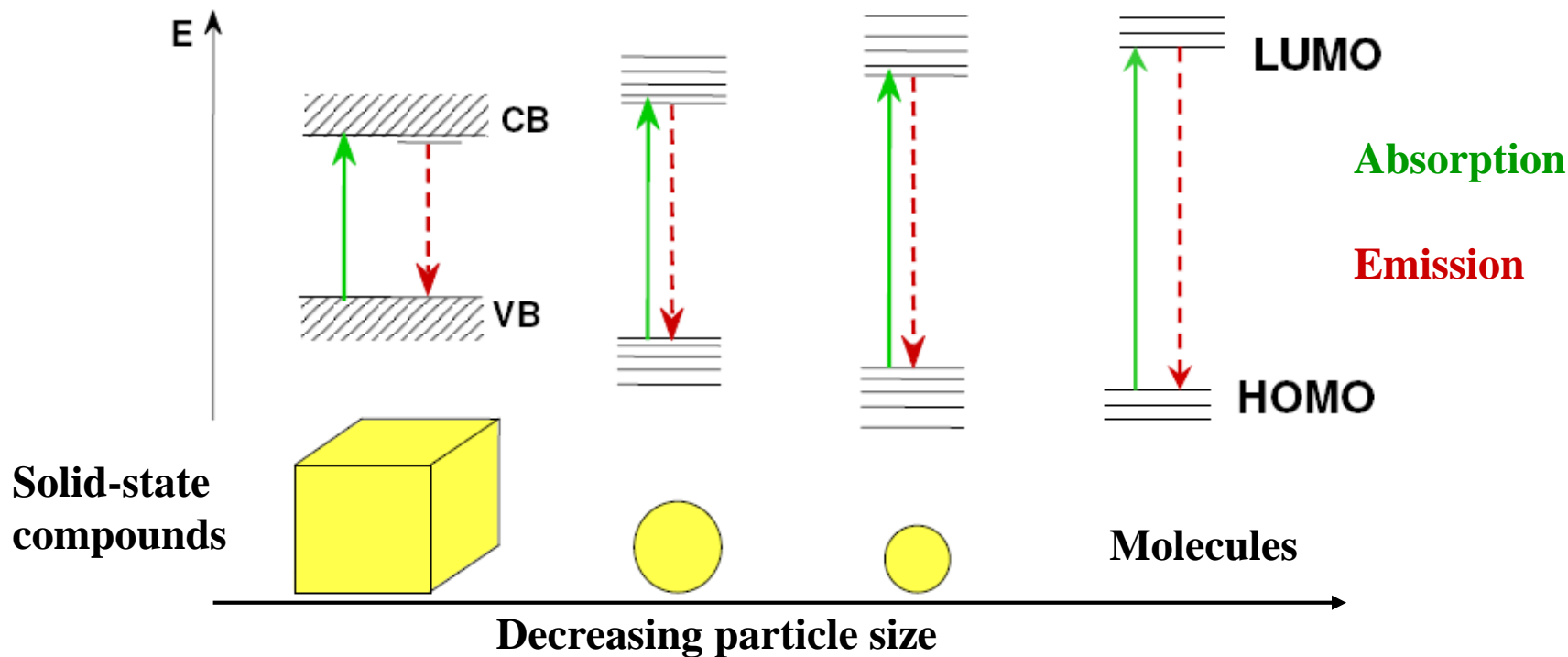
The Manifestation of Metallic Features depends on the Energy Gap of the Valence and Conduction Band



Intrinsic semi-conductors show electrical conductivity, if valence band electrons are thermally or optically promoted to the conduction band

11.5 Conductor, Intrinsic Semi-Conductor, Insulator

Band model – Dependence on Particle Size



CdS Nanoparticles: yellow → white

11.5 Conductor, Intrinsic Semi-Conductor, Insulator

The Band Gap depends on the chemical Composition, the EN-Difference, and the Structure Type

Substance	Structure type	Band gap E_G [eV]	EN-Difference
MgF₂	Rutile	12.0	2.9
MgO	Rock salt	7.8	2.3
Csp³	Diamond	5.3	0.0
AlP	Zinc blende	3.0	0.6
Si (amorphous)	-	1.7	0.0
Si (crystalline)	Diamond	1.1	0.0
ZnSe	Zinc blende	2.3	0.9
GaAs	Zinc blende	1.34	0.4
Ge	Diamond	0.72	0.0
InSb	Zinc blende	0.18	0.2
Grey tin	Diamond	0.08	0.0

Sn already becomes metallic at 13 °C → transition from α -Sn (grey) to β -Sn (white)

11.5 Conductor, Intrinsic Semi-Conductor, Insulator

The Conductivity of intrinsic Semiconductors can be enhanced by selective doping

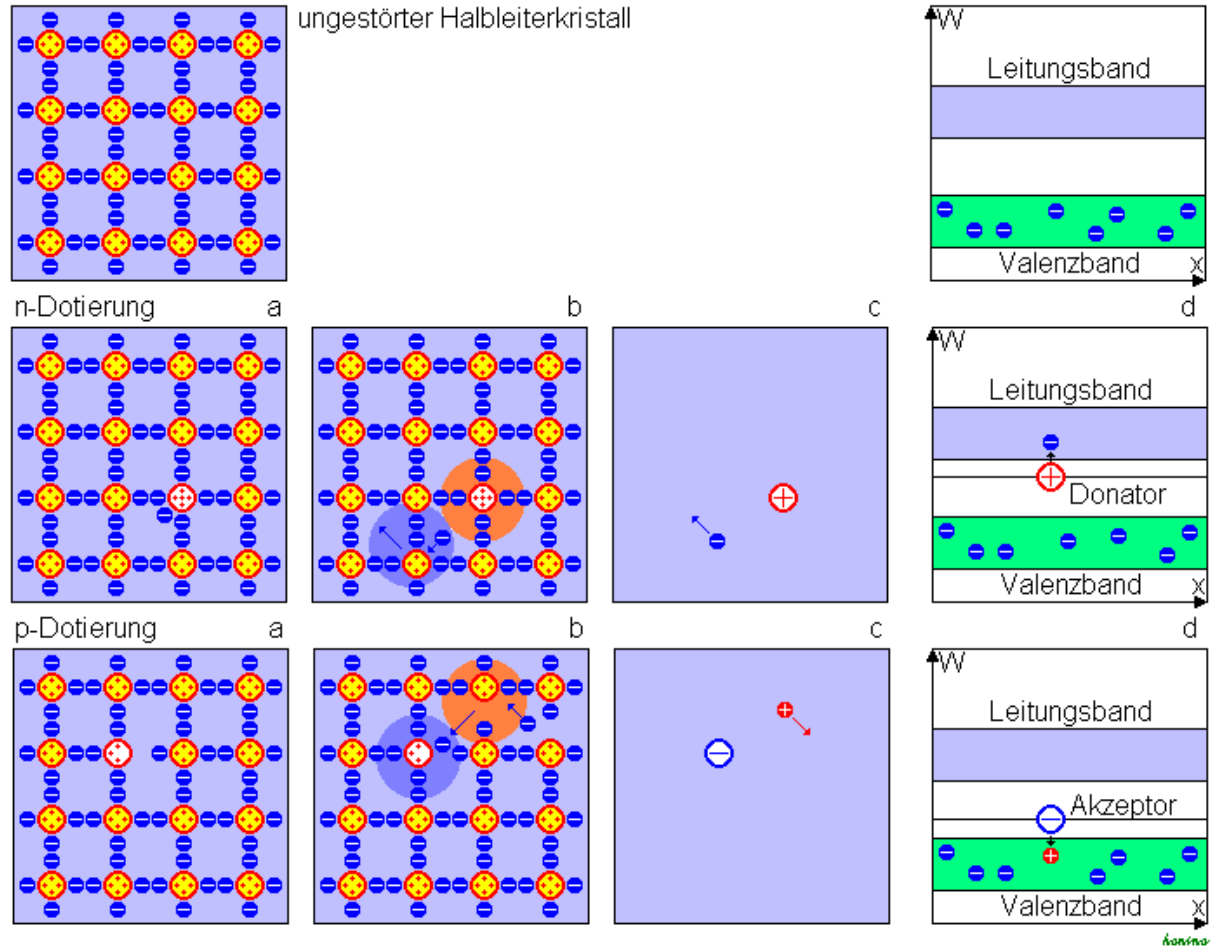
Doping, in this case, means the incorporation of defects into the crystal

Elements with deviating electronic structure lead to

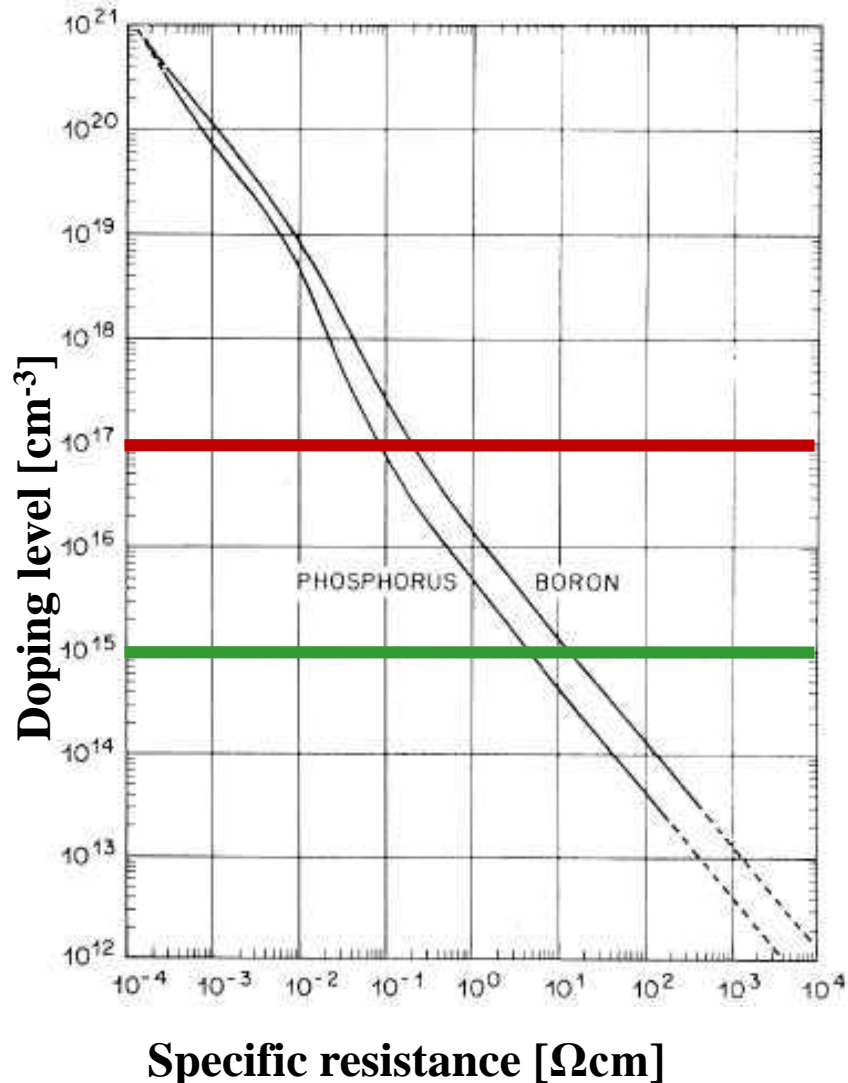
Electronic conduction
(→ n-doping)

or

Hole conduction
(→ p-doping)



11.5 Conductor, Intrinsic Semi-Conductor, Insulator



Example: Silicon

n-Doping (electronic conduction)

P, As, Sb (donators)

p-Doping (hole conduction)

B, Al, Ga, In (acceptors)

Electrical conductivity σ [S/m] is the reciprocal of the specific resistance

For semi-conductors: $\sigma = f(\text{doping level})$

Si 4.35×10^{-4} S/m

n-Si

1 ppm

9×10^2 S/m

p-Si

5×10^2 S/m

1 ppb

6×10^0 S/m

9×10^{-1} S/m

11.6 Doped Semi-Conductors

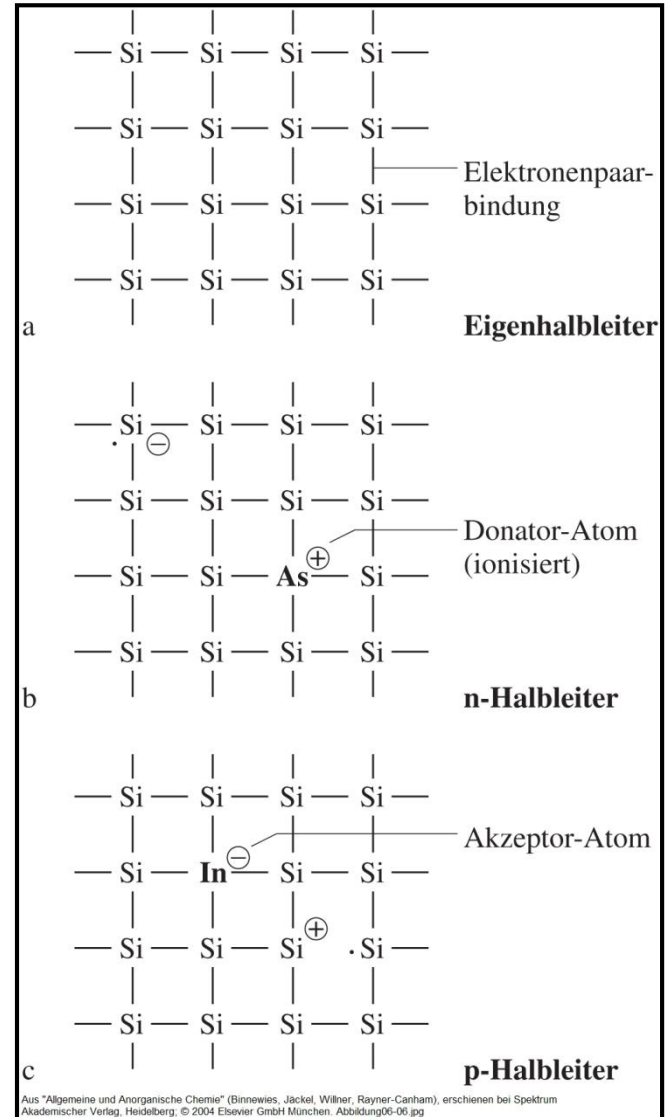
Silicon-Based Semiconductors

n-Semi-conductor: **Electron surplus**
P, As, Sb **5 outer electrons**
Si **4 outer electrons**

p-Semi-conductor: **Electron shortage**
B, Al, Ga, In **3 outer electrons**
Si **4 outer electrons**

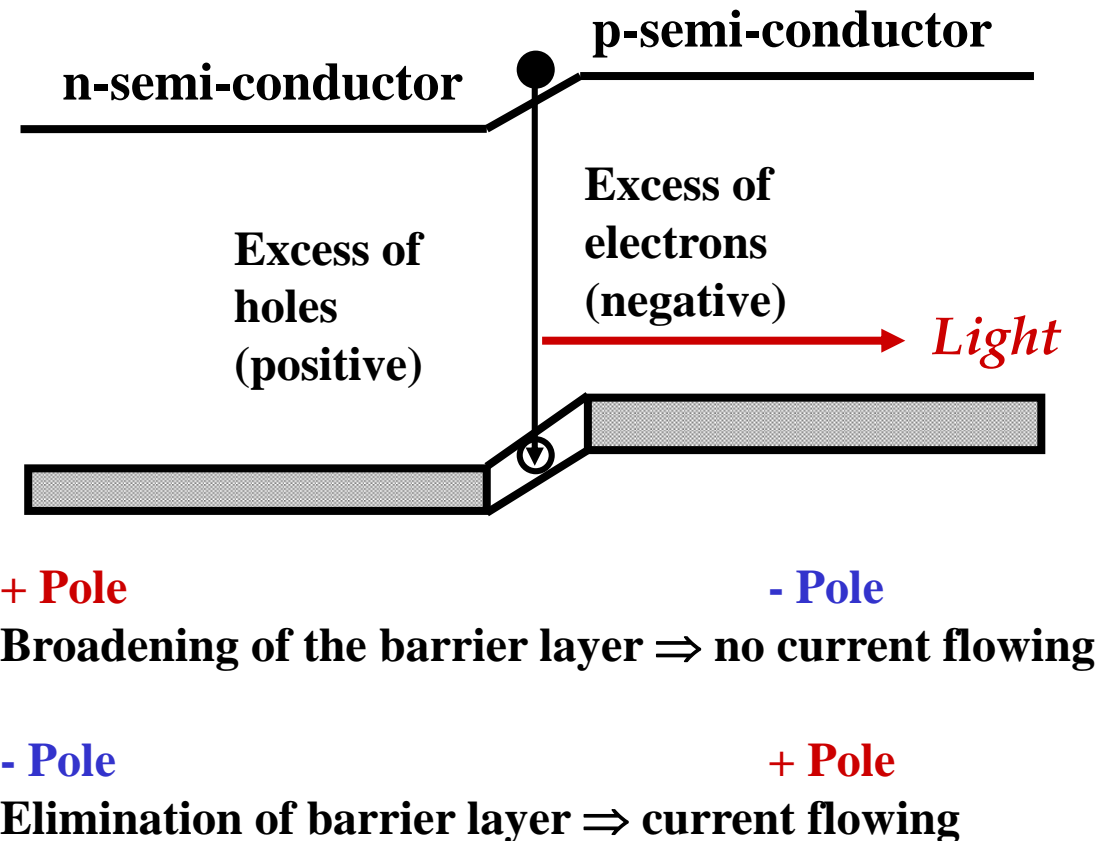
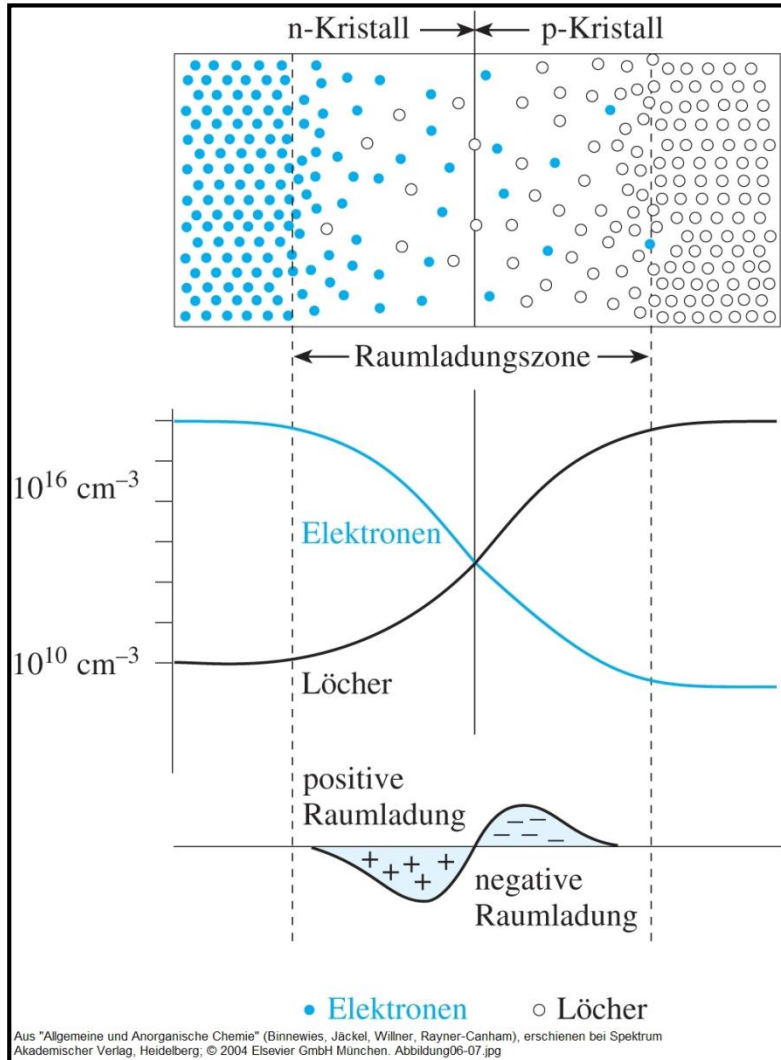
Applications

Diodes **Si**
Light emitting diodes **Si, AlN, GaN, InN,**
 AlP, GaP, InP, GaAs
Solar cells **Si, GaAs**
Transistors **Si**
ICs **Si, Ge**



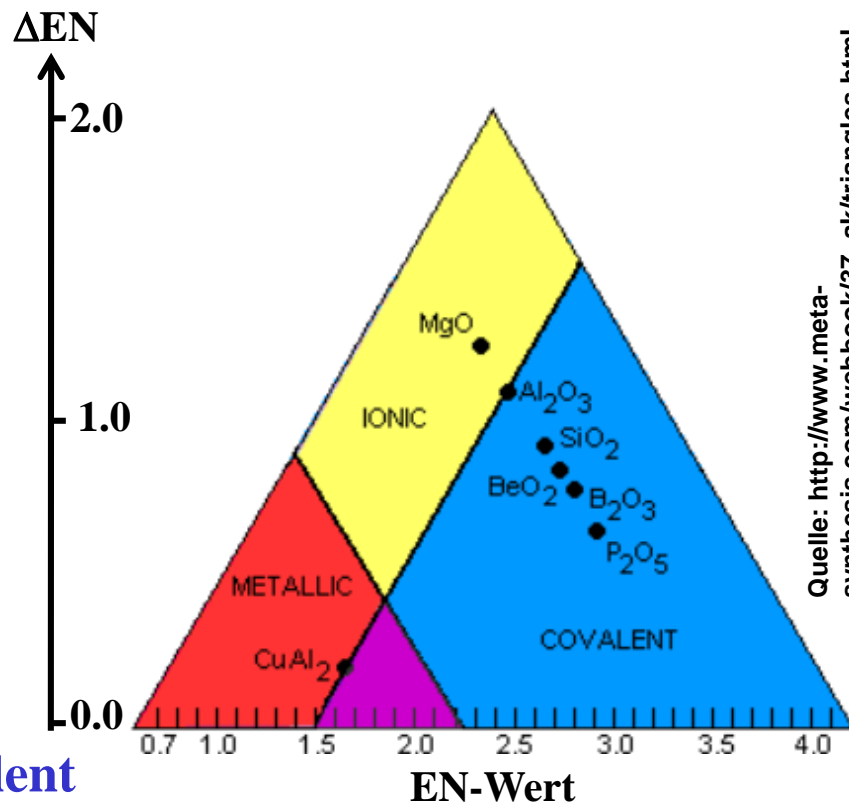
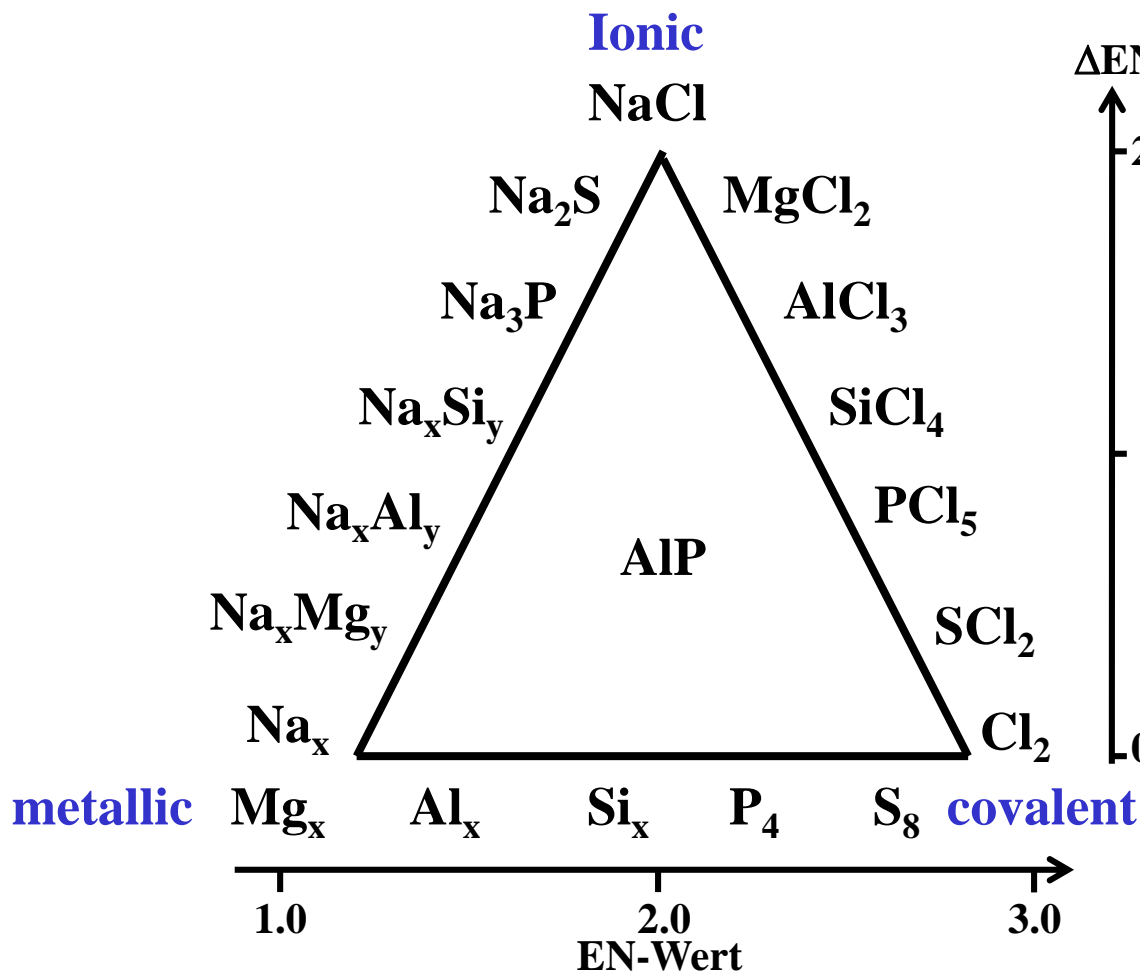
11.6 Doped Semi-Conductors

p/n-Transition = Barrier between n- and p-doped semiconducting Crystals



11.7 Comparison of Types of Bonding

The Bonding Triangle



Quelle: http://www.meta-synthesis.com/webbook/37_ak/triangles.html

AIP exhibits bonding characteristics of all three known types of bonding

11.7 Comparison of Types of Bonding

Bonding Trends for Elements of the 2nd and 3rd Period

Melting points and elemental compounds for elements of the 2. and 3. period

Li 181 °C	Be 1287 °C	B 2080 °C	C 3700 °C C ₆₀ , C ₇₀	N -210 °C N ₂	O -219 °C O ₂	F -220 °C F ₂	Ne -249 °C
Na 98 °C	Mg 650 °C	Al 660 °C	Si 1420 °C	P 44 °C P ₄	S 115 °C S ₈	Cl -101 °C Cl ₂	Ar -189 °C

- All half- and non-metal form bonds until they have reached an electronic octet
- Elements of the third period do not tend to form multiple bonds, since the bigger atomic radius hinders the overlap of the p-orbitals and thus the formation of π -bonds
⇒ Formation of oligomeric molecules such as P₄ or S₈

11.7 Comparison of Types of Bonding

Summary

The type of bond that dominates in a given compound essentially determines its chemical and physical properties

	Directed Interaction	Non-directed Interaction
Electrons localised	<i>Covalent bonding</i> $\Delta EN < 0.4$ H ₂ , Cl ₂ , CH ₄ , BrCl, CCl ₄ Polar covalent bonding $0.4 < \Delta EN < 1.7$ H ₂ O, NH ₃ , SO ₃	<i>Ionic bonding</i> $\Delta EN > 1,7$ NaCl, MgF ₂ , AlF ₃
Electrons delocalised	<i>∴</i>	<i>Metal bonding</i> Alkaline, Alkaline earth, and earth metals, transition metals, rare earth metals alloys

12. The Chemical Equilibrium

Contents

12.1 Preliminary Remarks

12.2 Law of Mass Action (LMA)

12.3 Principle of Le Chatelier

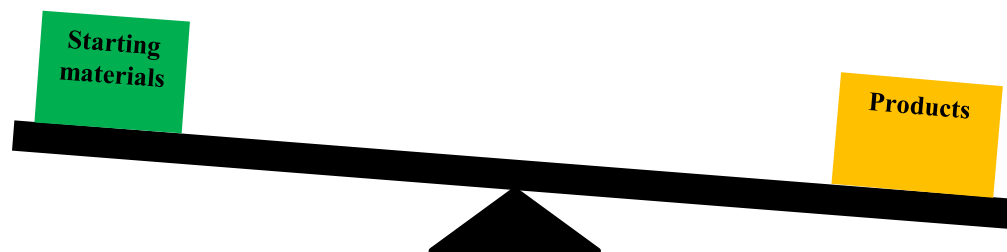
12.4 Solubility Equilibrium

12.5 Homogeneous Equilibria

12.6 Heterogeneous Equilibria

12.7 Coupled Equilibria

12.8 LMA and Chemical Energetics

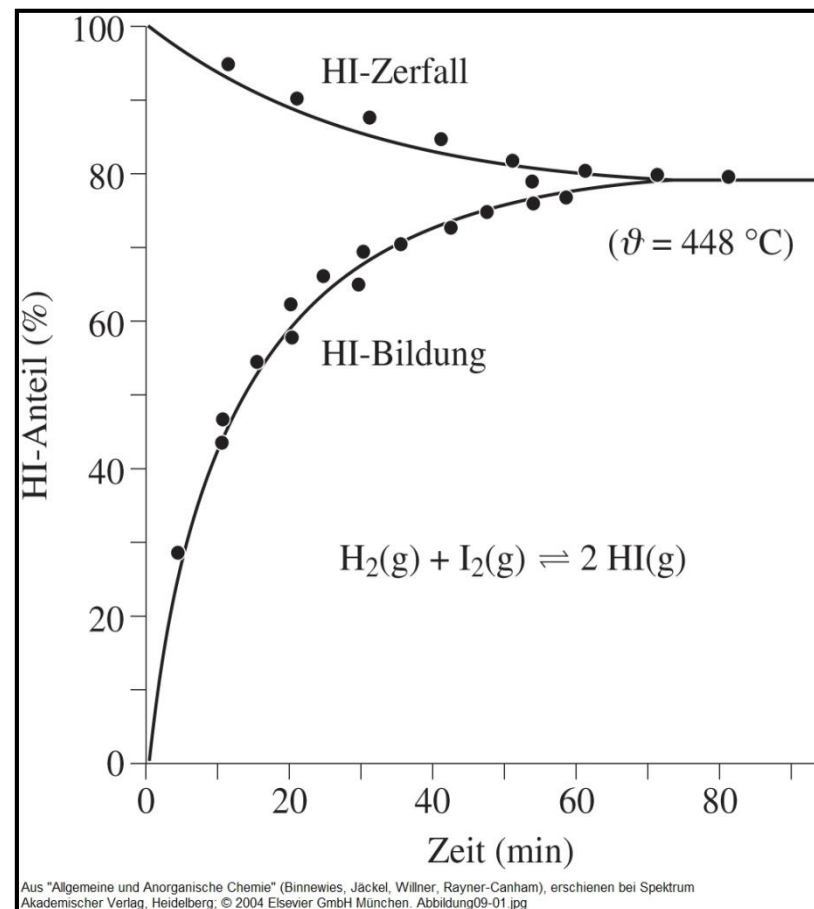


12.1 Preface

The Term Equilibrium pretends that there is an absolute Stability of dynamic Conditions! The Equilibrium State is no idle State but dynamic, whereby only Macroscopic changes can be described!

Examples

- **Biological equilibria:**
Rain forest (growth ↔ degradation)
- **Physical equilibria:**
Greenhouse (irradiation ↔ emission)
Stars (radiation pressure ↔ gravity)
- **Chemical equilibria:**
Reversible reactions, such as:
$$\text{C(s)} + \text{CO}_2\text{(g)} \rightleftharpoons 2 \text{CO(g)}$$
$$\text{SO}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)} \rightleftharpoons \text{SO}_3\text{(g)}$$
$$\text{CaCO}_3\text{(s)} \rightleftharpoons \text{CaO(s)} + \text{CO}_2\text{(g)}$$
$$\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2 \text{HI(g)}$$

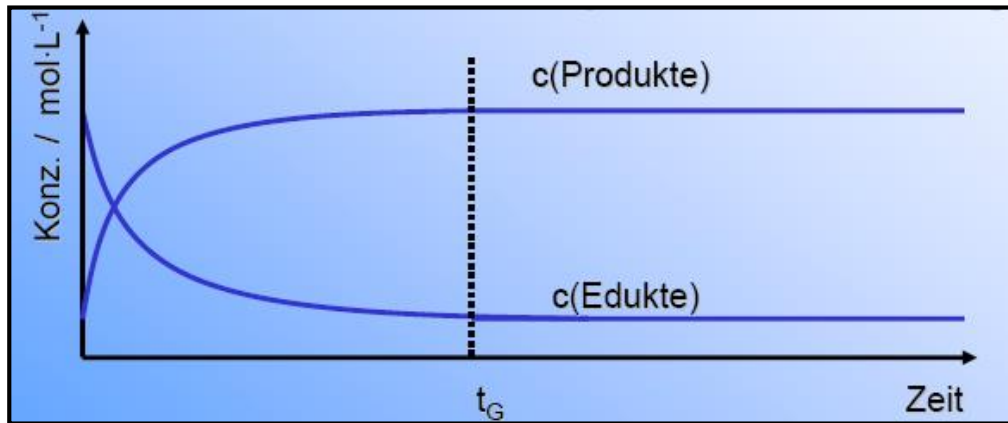


12.1 Preface

Equilibrium State

- Concentration of all participating substances remains constant
- Forward and back reactions run at the same time with equal speed, v

Equilibrium reaction between two reaction partners:



$$v_{\text{forw}} = k_{\text{forw}} \cdot c(\text{educts})$$

$$v_{\text{back}} = k_{\text{back}} \cdot c(\text{products})$$

$$\text{Equilibrium state: } v_{\text{forw}} = v_{\text{back}}$$

Establishing of an equilibrium takes time, t_G , and can be accelerated by a catalysator

12.2 Law of Mass Action (LMA)

Quantitative Description of Equilibrium Reactions

General formulation for reactions: $a A + b B \rightleftharpoons c C + d D$

Equilibrium constant
(Mass action constant)

$$K_c = \frac{c^c(C) \cdot c^d(D)}{c^a(A) \cdot c^b(B)}$$

for concentrations

$$K_p = \frac{p^c(C) \cdot p^d(D)}{p^a(A) \cdot p^b(B)}$$

for partial pressures

Example: $N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$ formation of nitrogen oxides in a combustion engine (endothermic reaction)

LMA formulates: $K_c(T) = c^2(NO) / (c^1(N_2) \cdot c^1(O_2))$

At 750 °C: 1 Vol-% NO $K_c = (0.01)^2 / (0.495)^2 = 0.41 \cdot 10^{-3} < 1$

At 2700 °C: 5 Vol-% NO $K_c = (0.05)^2 / (0.475)^2 = 11.1 \cdot 10^{-3} < 1$

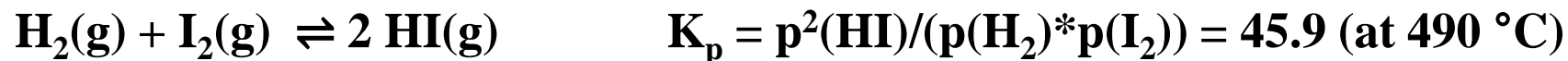
12.2 Law of Mass Action (LMA)

Correlation between the Course of the Reaction and K_c and K_p

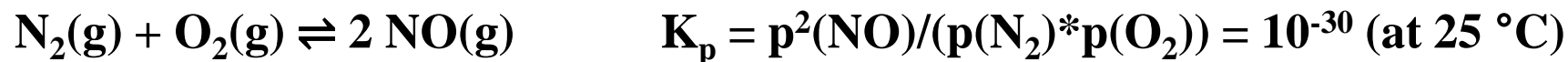
$K \gg 1$: Reaction proceeds almost entirely in favour of the products



$K \sim 1$: All reaction partner in similar concentrations



$K \ll 1$: Reaction does (almost) not take place



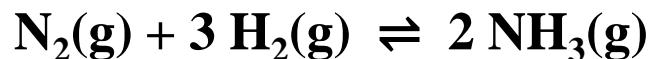
12.3 Principle of Le Chatelier

If Force, by Change of Either Pressure, Temperature or Concentration, Is Applied to a System in an Equilibrium State, the Equilibrium Can Be Readjusted so that the Applied Force Is Reduced

Affection of the equilibrium state of a chemical reaction by:

1. Change of concentration or the partial pressure, respectively
2. Change of temperature
3. Change of pressure (for reactions with gaseous components)

Example



Increase of temperature

Increase of pressure

Removal of product

$\Delta H = -92 \text{ kJ/mol}$, reduction of gaseous volume

\Rightarrow Equilibrium is shifted towards educts

\Rightarrow Equilibrium is shifted towards products

\Rightarrow Equilibrium is shifted towards products

12.4 Solubility Equilibria

Solubility Product used to describe the State of the Solubility Equilibrium of Salts

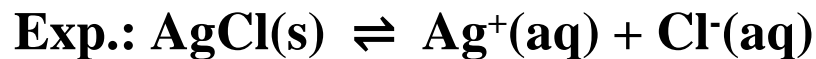


$$K = \frac{c^m(A^+) \cdot c^n(B^-)}{c(A_m B_n)}$$

Since the concentration of $A_m B_n$ at constant temperature is constant, the equation can be multiplied by $c(A_m B_n) \Rightarrow$ **Solubility product**

i.e. $K_L = K \cdot c(A_m B_n)$

$$K_L = c^m(A^+) \cdot c^n(B^-)$$



$$K_L = c(Ag^+) \cdot c(Cl^-) = 2 \cdot 10^{-10} \text{ mol}^2/\text{l}^2$$

$$pK_L = 9.7 \quad (p = -\log_{10})$$

Concentration of Ag^+ -ions: $c(Ag^+) = \sqrt{K_L} = 1.4 \cdot 10^{-5} \text{ mol/l}$, since $c(Ag^+) = c(Cl^-)$

12.4 Solubility Equilibria

Solubility Product of poorly soluble Salts

Salts	pK _L -values (in reference to activities)	
PbCl ₂	4.8	
Hg ₂ Cl ₂	17.9	HCl-group
AgCl	9.7	
PbS	27.5	
HgS	52.7	H ₂ S-group
CuS	36.1	
NiS	19.4	
MnS	10.5	(NH ₄) ₂ S-group
FeS	18.1	
BaCO ₃	8.3	
SrCO ₃	9.0	(NH ₄) ₂ CO ₃ -group
CaCO ₃	8.4	

Experimental investigations of the solubility of salts show that the solubility depends on the concentrations of the salt itself and impurity salts

$$\text{Activity: } a = \gamma \cdot c$$

(effective concentration)

Highly diluted solutions

$$\gamma \approx 1.0 \quad \text{with } a = c$$

Concentrated solutions

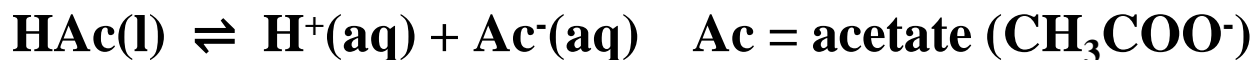
$$\gamma = 0.0 \dots 1.0 \quad \text{with } a < c$$

The value of the activity coefficient depends on the ionic strength, the ionic charge and the ionic radius

12.5 Homogeneous Equilibria

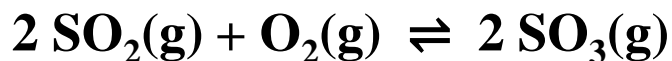
Equilibria Are Called Homogeneous, if all Reaction Partners Are of the Same Phase (Solution or Gaseous Phase)

In solutions

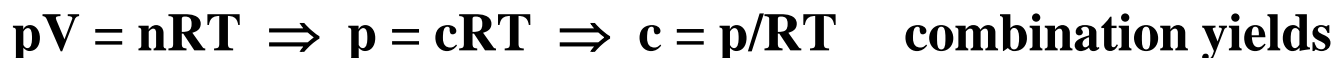


$$K_c = \frac{c(\text{H}^+) \cdot c(\text{Ac}^-)}{c(\text{HAc})}$$

In gaseous phase



$$K_c = \frac{c^2(\text{SO}_3)}{c^2(\text{SO}_2) \cdot c(\text{O}_2)}$$



$$K_p = \frac{p^2(\text{SO}_3)}{p^2(\text{SO}_2) \cdot p(\text{O}_2)} RT$$

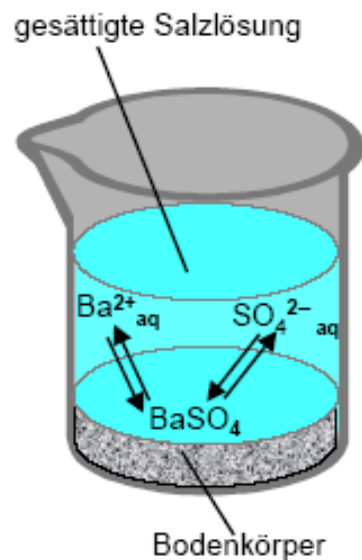
General relation between K_p and K_c

(Δv is the difference of the number of particles between the product and educt side)

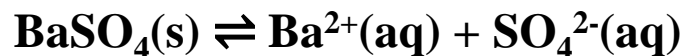
$$K_p = K_c \frac{1}{(R \cdot T)^{\Delta v}}$$

12.6 Heterogeneous Equilibria

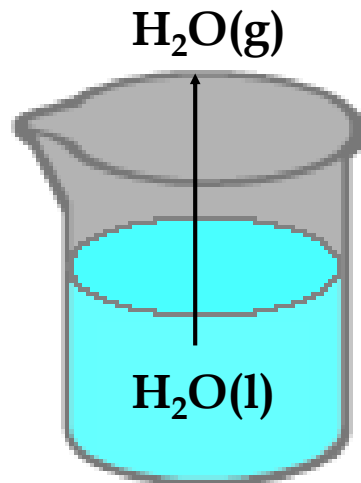
Equilibria Are Called Heterogeneous, if the Reaction Partners Possess Different Physical Phases



Solubility equilibria



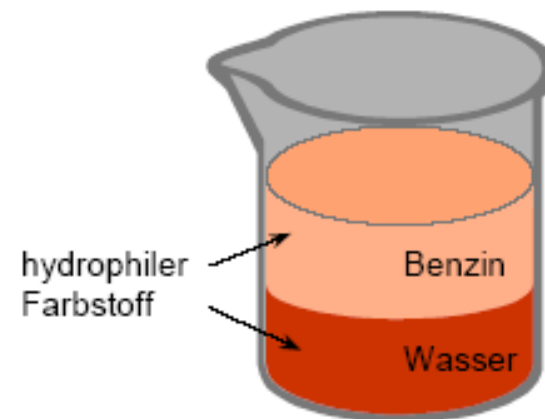
$$K = K_L = c(\text{Ba}^{2+}) \cdot c(\text{SO}_4^{2-})$$



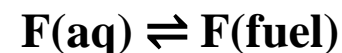
Phase equilibria



$$K_p = p(\text{H}_2\text{O})$$



Distribution equilibria



$$K = c(F_{\text{fuel}})/c(F_{\text{aq}})$$

(Nernst's law of distribution)

12.7 Coupled Equilibria

Chemical Reactions Are often Accompanied by Side or Follow-up Reactions

Example: Precipitation of AgCl through addition of NaCl to a solution of AgNO_3



$$K_L = c(\text{Ag}^+) \cdot c(\text{Cl}^-) = 2 \cdot 10^{-10} \text{ mol}^2/\text{l}^2$$

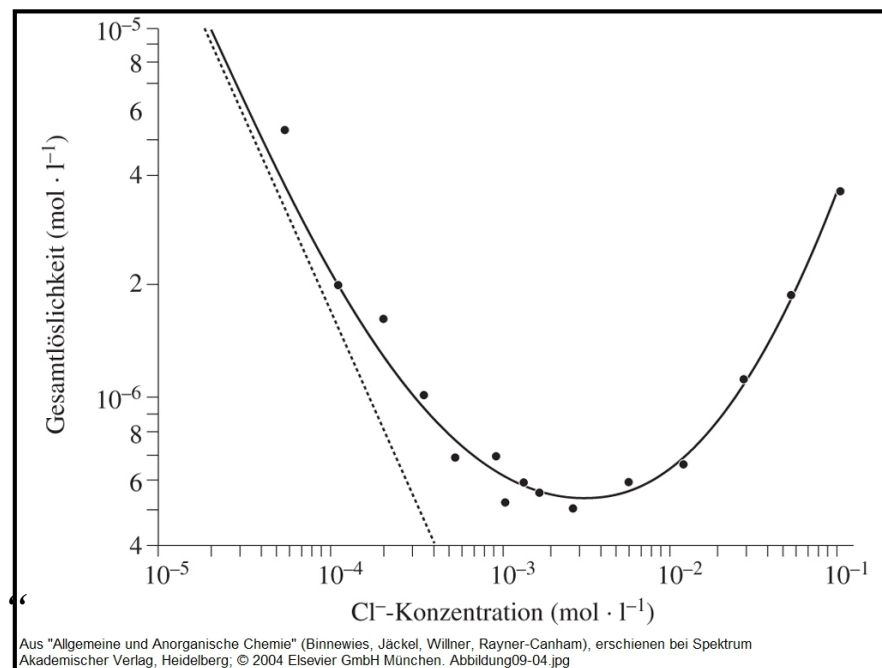


$$K = \frac{c([\text{AgCl}_2]^{-})}{c(\text{Ag}^+) \cdot c^2(\text{Cl}^-)} = 1.6 \cdot 10^{-5} \text{ l}^2/\text{mol}^2$$

At higher concentrations the formation of the chloro complex dominates:



$$K_C = \frac{c([\text{AgCl}_2]^{-})}{c(\text{Cl}^-)} = K_L \cdot K \quad \text{“Product of the equilibrium constants”}$$



12.8 LMA and Chemical Energetics

The Position of the Equilibrium Can Be Derived from the Thermodynamic Quantities Enthalpy H and Entropy S

Free standard reaction enthalpy: $\Delta G^0 = \Delta H^0 - T\Delta S^0$

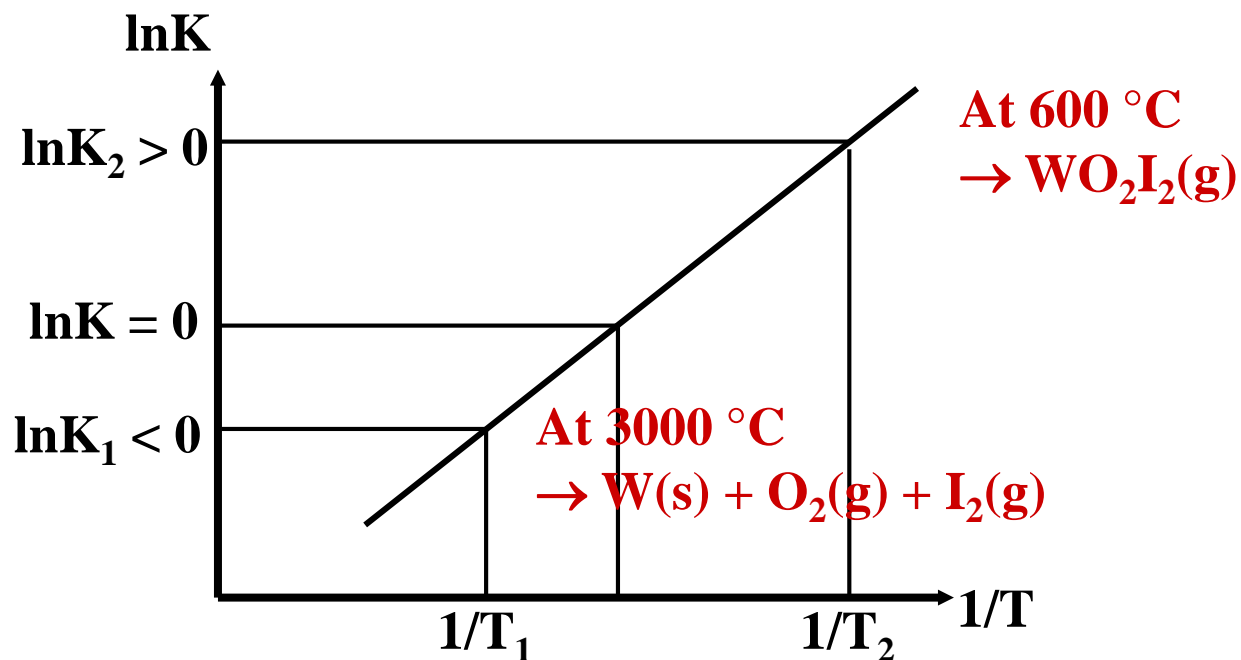
$$\ln K = - \Delta G^0 / RT$$

Insertion yields
van't Hoff's equation:

$$\ln K = - \frac{\Delta H^0}{R \cdot T} + \frac{\Delta S^0}{R}$$

The position of the equilibrium or K is thus dependent on the temperature

$W + O_2 + I_2 \rightleftharpoons WO_2I_2$ "W-recycling in halide lamps"



13. Acids and Bases

Contents

13.1 Historical Background

13.2 Definitions

13.3 Strength of Acids and Bases

13.4 Excursus: Super Acids

13.5 Acid-Base Titrations

13.6 Buffer

13.7 Isoelectric Point

13.8 Electrophoretic Precipitation

13.9 Summary



13.1 Historical Background

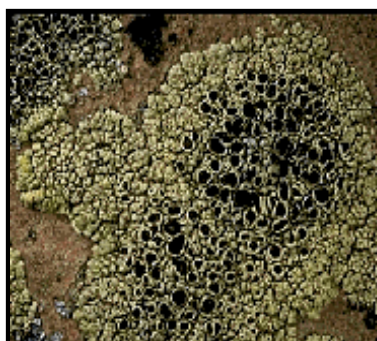
Acids

- Taste acidic
 - Citric acid, acetic acid
 - Hydrochloric acid, phosphoric acid
- Dissolve non-noble metals upon release of hydrogen
- Colour plant dyes red (red cabbage, litmus test)
→ Concept of acids (**R. Boyle, 1663**)

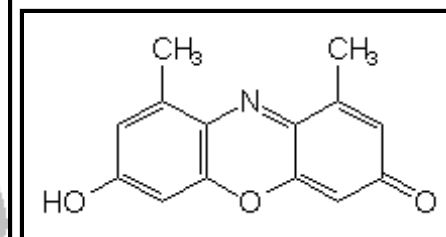
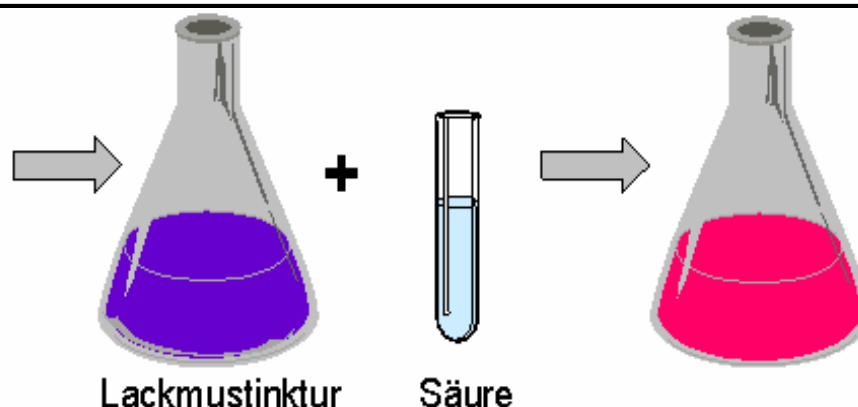
Bases

- Taste bitter or soapy
- Yield basic or alkaline solutions (leach)
- Dissolve some organic substances by saponification
- React with acids to form salts and water

Rocella tinctoria



Flechten



Orcein

13.2 Definitions - Arrhenius (1884)

Acidic Properties Are Based on H⁺-Ions, whilst Basic Properties Are Mediated by OH⁻-Ions

Acids dissociate in water and form H⁺-ions:

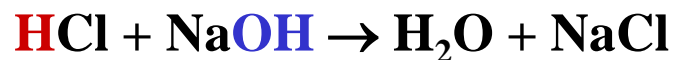
- **HCl → H⁺ + Cl⁻**
- **H₂SO₄ → 2 H⁺ + SO₄²⁻**

Bases dissociate in water and form OH⁻-ions:

- **NaOH → Na⁺ + OH⁻**
- **Ba(OH)₂ → Ba²⁺ + 2 OH⁻**

Neutralisation: H⁺ + OH⁻ → H₂O

ΔH = -57.4 kJ/mol



Problem

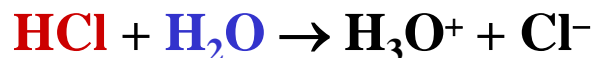
According to this definition NH₃ is no base, although it reacts as a base:

- **NH₃ + H₂O → NH₄⁺ + OH⁻**

13.2 Definitions - Brønsted and Lowry (1923)

Acid/Base-Reactions Are Proton Transfer Reactions (in Water)

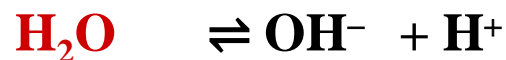
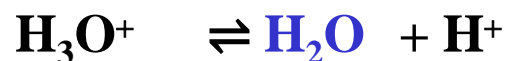
Acids are substances that transfer protons to their reaction partners:



Bases are substances that accept protons from their reaction partners:



Conjugated acid-base-pairs:



- In proton transfer reactions always two pairs of acid-base-pairs are required
- H_2O reacts acidic or basic depending on the reaction partner (ampholyte)
- The assignment as acid or base depends on the reaction partner

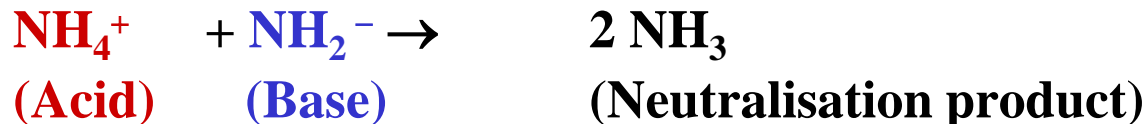
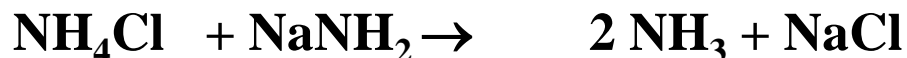
13.2 Definitions - Brønsted and Lowry (1923)

The Lowry/Brønsted Concept of Acids and Bases Includes Reactions without Solvents (Gaseous Phase) and other Protic Solvents

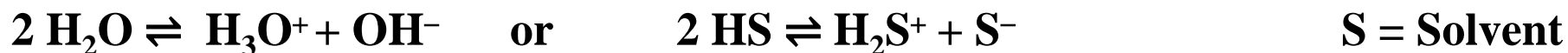
In gaseous phase:



In liquid ammonia as solvent:



In protic solvents with auto-protolysis act



- 1) substances that increase the **cation concentration** of the solvent, as **acid**
- 2) Substance that increase the **anion concentration** of the solvent, as **base**

13.2 Definitions – Solvent Systems

Acids and Bases in Solvent Systems with Autoprotolysis

Solvent	\rightleftharpoons	Acidic-Ion	+	Base-Ion	Acid	Base
H ₂ O		H ₃ O ⁺		OH ⁻	HCl	NaOH
NH ₃		NH ₄ ⁺		NH ₂ ⁻	NH ₄ Cl	NaNH ₂
CH ₃ COOH		CH ₃ COOH ₂ ⁺		CH ₃ COO ⁻	HCl	CH ₃ COONa
SO ₂		SO ²⁺		SO ₃ ²⁻	SOCl ₂	Na ₂ SO ₃

The autoprotolysis constant K_{HS} describes the degree of intrinsic dissociation:

$$K_{HS} = [H_2S^+][S^-]$$

$$K_{H_2O} = [H_3O^+][OH^-] = 10^{-14} \text{ mol}^2/\text{l}^2 = K_w = \text{Ionic product of water at } 25 \text{ }^\circ\text{C}$$

$$K_{NH_3} = [NH_4^+][NH_2^-] = 10^{-29} \text{ mol}^2/\text{l}^2$$

$$\text{At neutral point: } [H_2S^+] = [S^-] \Rightarrow K_{HS} = [H_2S^+]^2 \Rightarrow [H_2S^+] = \sqrt{K_{HS}}$$

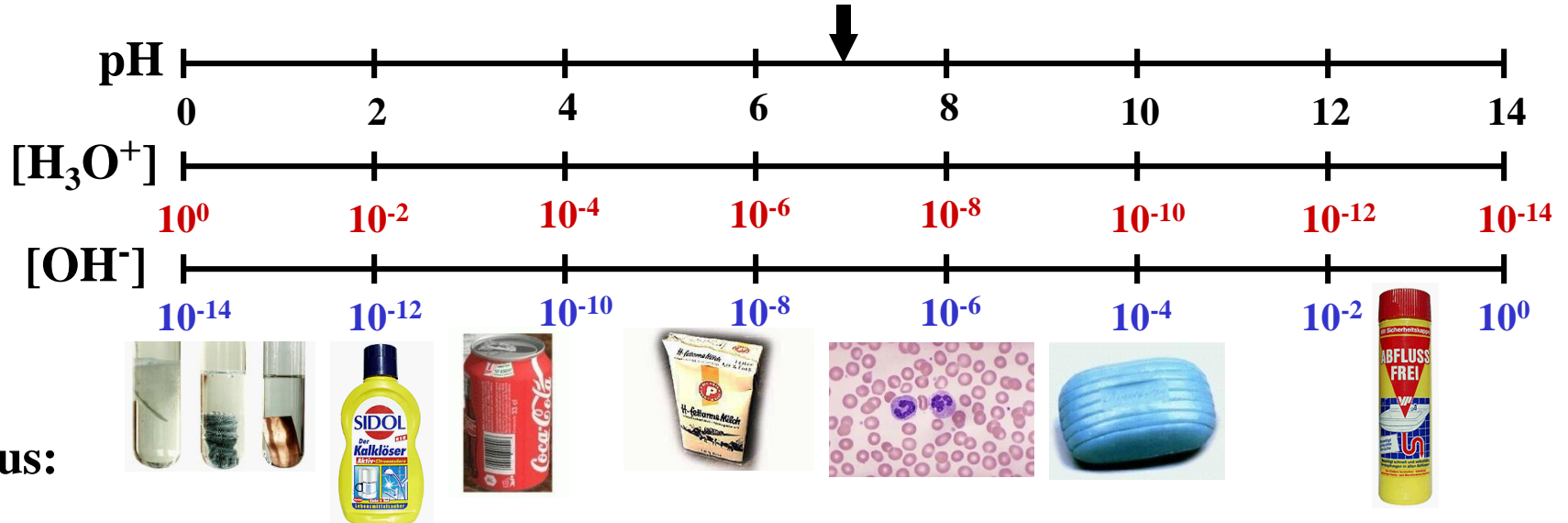
13.2 Definitions - pH-Value

The pH-Value Is Defined as the Negative Decadic Logarithm of the H_3O^+ -Ion Concentration

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

pH = French: puissance d'hydrogène (S.P.L. Sørensen, 1909)

Neutral point: $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ mol/l} \Rightarrow \text{pH} = 7$



Analogous:

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

In aqueous solutions the product of the concentrations of the H_3O^+ and OH^- Ions is constant: $\text{pH} + \text{pOH} = 14$

13.2 Definitions - Lewis (1938)

During Acid-Base Reactions Pairs of Electrons Are Being Transferred

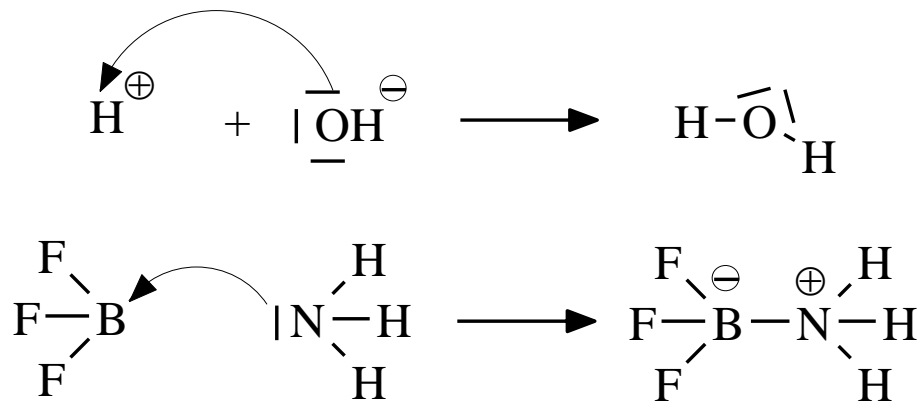
Acids acts as acceptors for electron pairs (electrophiles):

BF₃, SiF₄, SO₂, SO₃, Mg²⁺, Al³⁺, H⁺ ⇒ Electron-deficient compounds

Bases donate electron pairs (nucleophiles):

NH₃, PH₃, CO, N₂, NO, F⁻, CN⁻, OH⁻ ⇒ free pairs of electrons

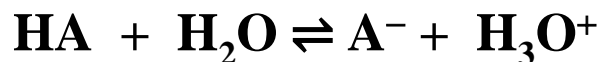
Reaction examples: **Acid** + **Base** neutralisation product



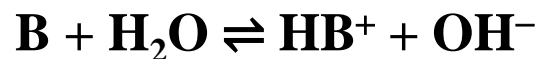
13.3 Strength of Acids and Bases

According to Brønsted/Lowry the Strength of an Acid/Base Depends on Its Dissociation Degree in a Given Solvent (Water)

Reaction of an acid with water



Reaction of a base with water



The equilibrium ratios are given by the law of mass action:

$$K^*[\text{H}_2\text{O}] = K_A = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

$$K^*[\text{H}_2\text{O}] = K_B = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

$$\text{p}K_A = -\log K_a$$

$$\text{p}K_B = -\log K_B$$

K_A = acid constant

K_B = base constant

In water the strongest acid is the H_3O^+ -ion, the strongest base the OH^- -ion

13.3 Strength of Acids and Bases

Brønsted Acids and Bases Can Be Assigned to a Protochemical Series

Acid	\rightleftharpoons	Base	+ H ⁺	pKa-Value	Name
HClO ₄		ClO ₄ ⁻	+ H ⁺	-10	Perchloric acid
HCl		Cl ⁻	+ H ⁺	-7	Hydrogen chloride
H ₂ SO ₄		HSO ₄ ⁻	+ H ⁺	-3	Sulphuric acid
HNO ₃		NO ₃ ⁻	+ H ⁺	-1.4	Nitric acid
H ₃ O ⁺		H ₂ O	+ H ⁺	0	Hydronium-ion
H ₃ PO ₄		H ₂ PO ₄ ⁻	+ H ⁺	2.2	Phosphoric acid
CH ₃ COOH		CH ₃ COO ⁻	+ H ⁺	4.75	Acetic acid
H ₂ S		HS ⁻	+ H ⁺	7.2	Hydrogen sulphide
NH ₄ ⁺		NH ₃	+ H ⁺	9.25	Ammonium-ion
H ₂ O		OH ⁻	+ H ⁺	14	Water

Acidic strength

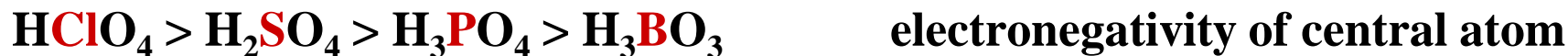
Dissociation degree of an acid in water:

$$\text{Dissociation} = \frac{100}{1 + 10^{(\text{pKa} - \text{pH})}} [\%]$$

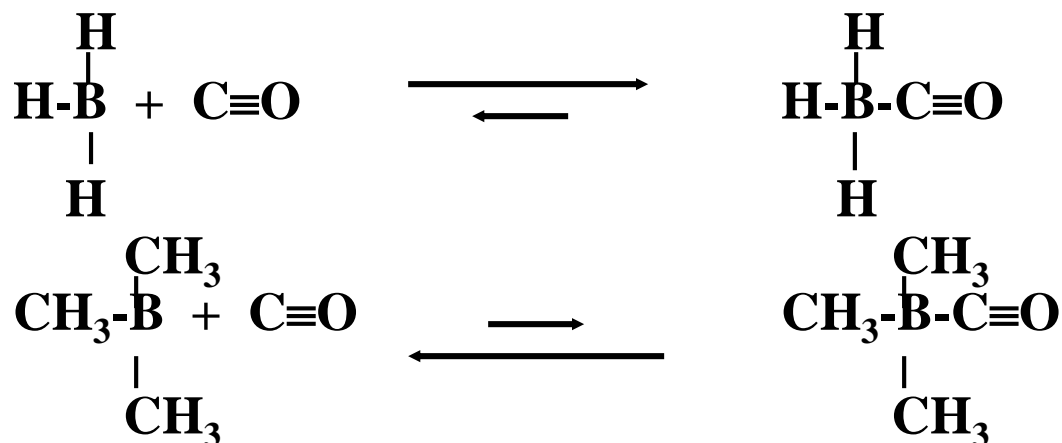
13.3 Strength of Acids and Bases

The Strength of Acids and Bases Is Determined by the Polarity of Covalent Element-H Bonds, Sterical Effects and Solvation

Polarity of the element-H bond (O-H bond)



Sterical effects (Lewis acid-base reactions)



Sterically demanding groups
(methyl groups) change the
equilibrium

13.3 Strength of Acids and Bases - Indicators

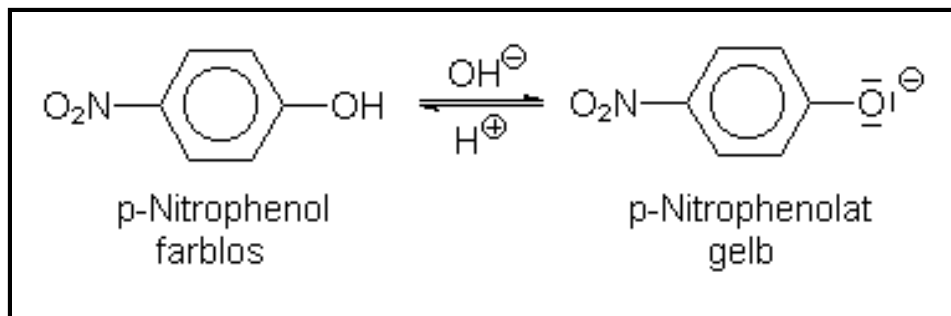
(Acid-Base-)Indicators are weak organic Acids or Bases which Solutions change their Colour upon Change of the pH



$$K_{\text{Ind}} = \frac{[\text{H}_3\text{O}^+][\text{Ind}^-]}{[\text{HInd}]}$$

$$\text{pH} = \text{p}K_{\text{Ind}} - \log \frac{[\text{HInd}]}{[\text{Ind}^-]}$$

Colour transition range: $\text{pH} = \text{p}K_{\text{Ind}} \pm 1$

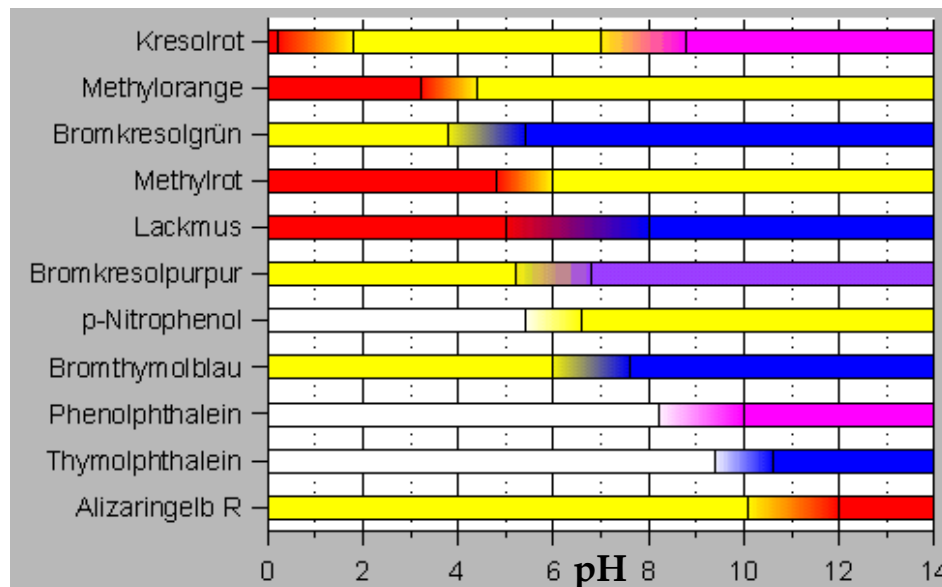


absorbs UV

absorbs blue

Mixed indicators

Litmus, universal indicator, red cabbage



13.4 Excursus: Super Acids

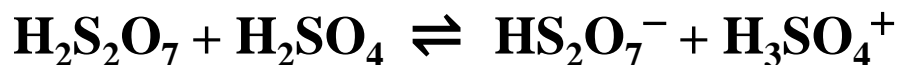
Super Acids are Compositions that are more Acidic than 100% Sulphuric Acid

Pure sulphuric acid exhibits auto-protolysis



Indicator base, e.g. p-nitroaniline

Super acids increase the concentration of H_3SO_4^+ -cations:



SbF_5 increases even the strength of HSO_3F

Measurements by Hammett (1930)

Use of weak indicator bases

for determination

$$H_0 = \text{p}K_{\text{A,Ind}} - \log \frac{[\text{HInd}]}{[\text{Ind}^-]}$$

$$1 \text{ M } \text{H}_2\text{SO}_4 \quad H_0 = -2.5$$

$$\text{H}_2\text{SO}_4 \quad H_0 = -12$$

$$\text{H}_2\text{S}_2\text{O}_7 \quad H_0 = -15$$

$$\text{HSO}_3\text{F} \quad H_0 = -15$$

$$\text{HSO}_3\text{F}/\text{SbF}_5 \quad H_0 = -21.5$$

A mixture of SbF_5 and HSO_3F is 10^{10} times more acidic than pure sulphuric acid!

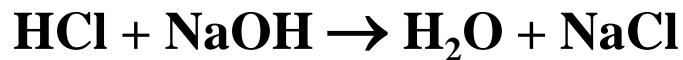
13.5 Acid-Base Titrations

Acid-Base Titrations are used to determine the Concentration of an Acid or Base in aqueous Solution

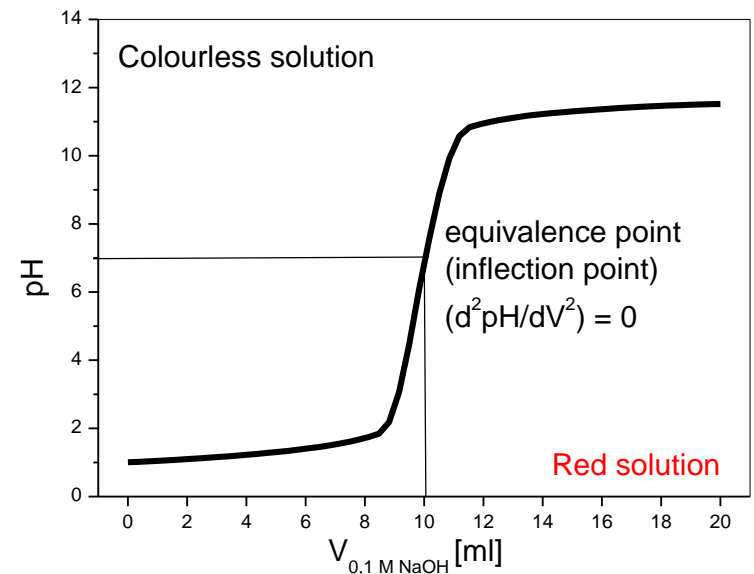
Titration of a strong acid (HCl) with a strong base (NaOH)

Analyte: 10 ml 0.1 M HCl

Titrant: x ml 0.1 M NaOH is added



The equivalent point is reached, as soon as 10 ml 0.1 M NaOH are added



- **Visualisation of the equivalent point is achieved by the addition of an indicator, e.g. phenolphthalein**
- **For strong acids and bases is true: the equivalent point is at pH = 7.0**

13.6 Buffer

Buffer are Solutions which pH Value does hardly change upon Addition of an Acid or Base

Buffer are mixtures of a

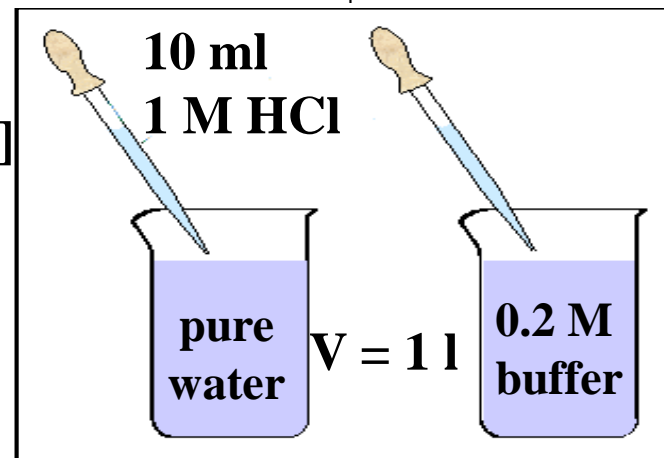
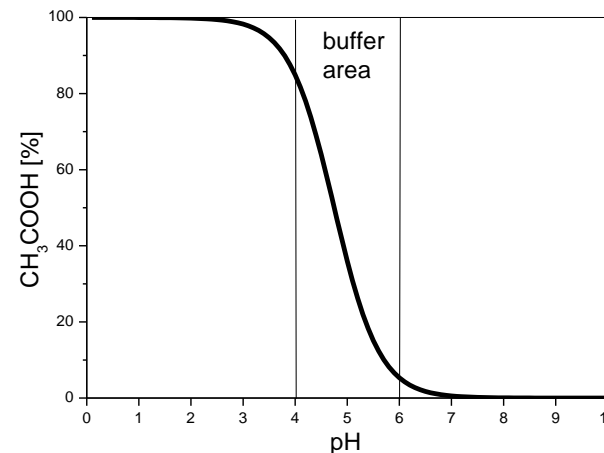
- Weak acid and its salt
- Weak bases and its salt



$$K_A = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \text{pH} = \text{p}K_A + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\text{pH} = \text{p}K_A + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Henderson-Hasselbalch-equation



Start pH	7.0	4.8
End pH	2.0	4.71

13.6 Buffer - Blood

A constant pH-Value of Blood is maintained by Multiple Buffer Systems

pH of blood plasma (human)

pH = 7.4 ± 0.03

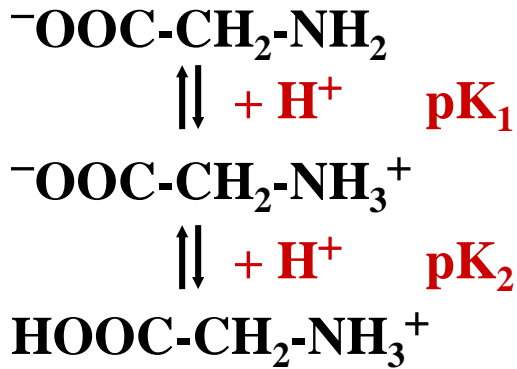


<u>Buffer System</u>	<u>pK_A</u>	<u>Name</u>	<u>Buffer Capacity</u>
$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_3^-$	6.1	Carbonate	75%
$\text{HbH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Hb}$	8.25	Haemoglobin	24%
$\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$	6.8	Phosphate	1%

13.7 Isoelectric Point

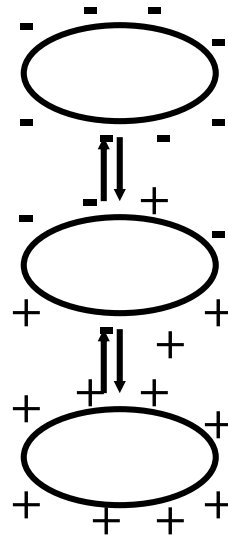
The Isoelectric Point (IEP) is the pH-Value, whereat the average electrical Charge of a polyprotic Acid is zero

Amino acid

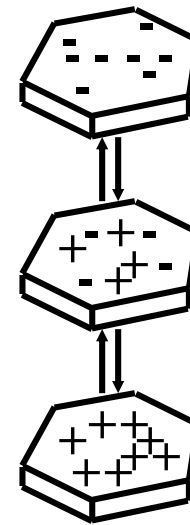


IEP at $\text{pH} = (\text{pK}_1 + \text{pK}_2)/2$

Proteins (nano particle)



Powder (micro particle)



**Particles with neutral surface
 \Rightarrow Point of Zero Charge PZC**

Application in

- Analytical chemistry
- Coating technology

**electrophoreses, amino acid analysis
 electrophoretic deposition of particles**

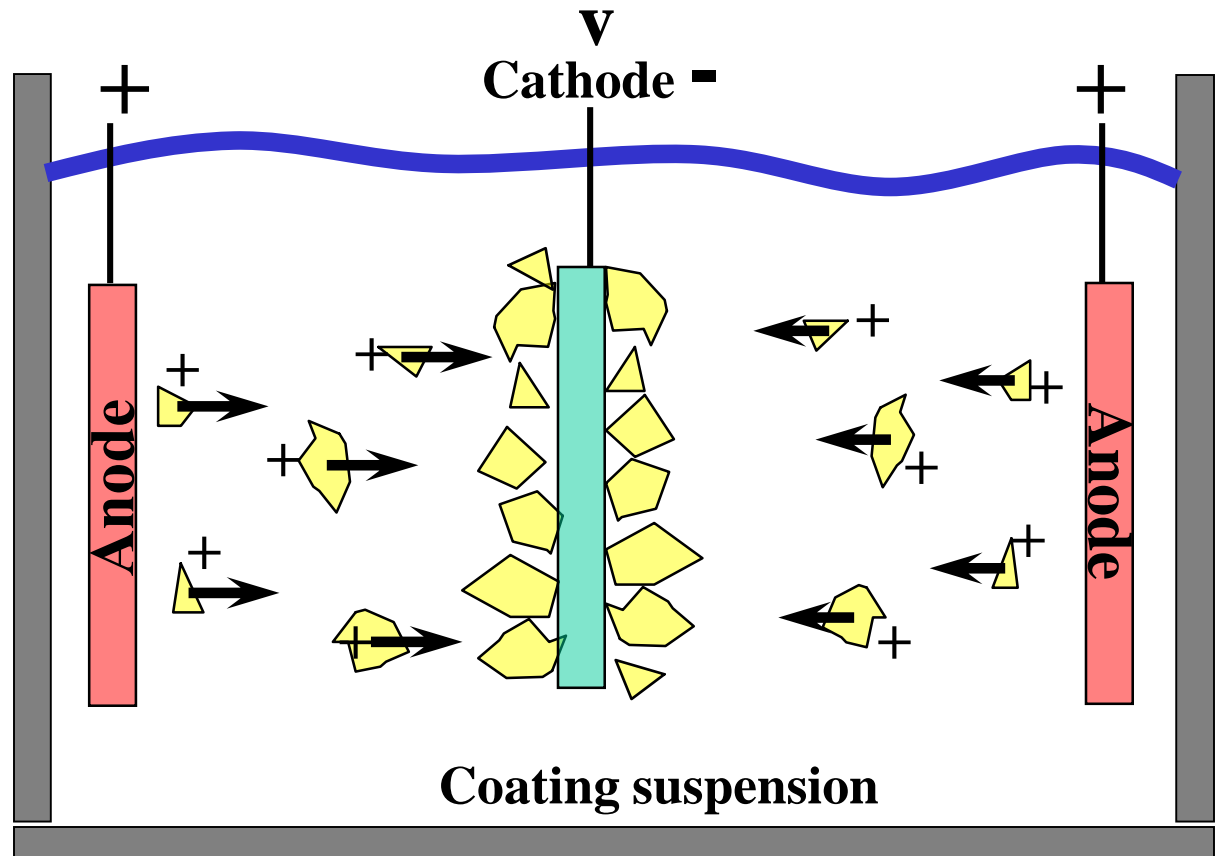
13.8 Electrophoretic Deposition

The Surface Charge of a Particle in Suspension is determined by the pH-Value (or by the Addition of an Electrolyte, e.g. Dodecyl Sulphate)

<u>Compound</u>	<u>PZC at [pH]</u>
SiO ₂	2.5
TiO ₂	4.5
Al ₂ O ₃	9.0
Y ₂ O ₃	9.1
Yb ₂ O ₃	9.7
La ₂ O ₃	10.4
MgO	12.0

Example

The surface of Al₂O₃-particles at pH < 9.0 is positively charged



13.9 Summary

Fundamental similarities of all acid-base definitions

- An **acid** is a compound that cleaves positively charged species or takes up a negatively charged species
- A **base** is a compound that cleaves a negatively charged species or takes up a positively charged species

Basic definitions

- **Acidity** describes the positive character of a chemical species, which is reduced through the reaction with a base
- **Basicity** describes the negative character of a chemical species which is decreased through a reaction with an acid

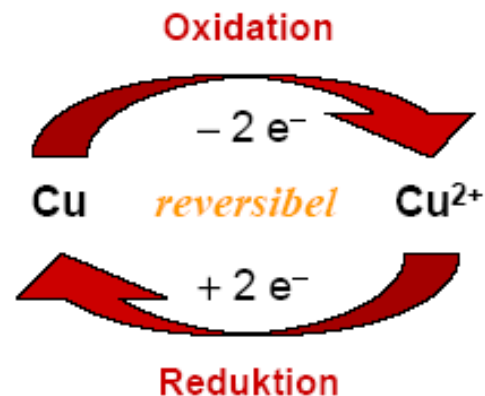
Strength of acids and bases

- The strength depends on the charge density (charge per volume)
- Strongest **acid**: proton **H⁺** (size $\sim 10^{-13}$ cm)
- Strongest **base**: electron **e⁻** (elemental particle)

14. Redox Reactions

Contents

- 14.1 Oxidation Numbers
- 14.2 Oxidation and Reduction
- 14.3 Set Up of Redox Equations
- 14.4 Galvanic Elements
- 14.5 Calculation of Redox Potentials
- 14.6 Standard Hydrogen Electrode
- 14.7 Electrochemical Series
- 14.8 Electrolysis
- 14.9 Galvanic Voltage Source
- 14.10 Corrosion- and Corrosion Inhibition



14.1 Oxidation Numbers

General Rules to determine Oxidation Numbers

1. Elements

The oxidation number of an atom in its elemental form is zero

2. Ionic compounds

The oxidation numbers are identical to the charge of the ion

Compound	Ions	Oxidation number
NaCl	Na ⁺ , Cl ⁻	Na ^{+I} Cl ^{-I}
Fe ₃ O ₄	Fe ²⁺ 2 Fe ³⁺ , 4 O ²⁻	Fe ^{+II/+III} O ^{-II}

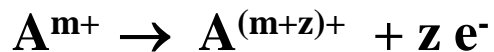
3. Covalent compounds

The oxidation numbers of the atoms are determined by heterolysis

Compound	Lewis structure	Fictive ions	Oxidation number
HCl	H-Cl	H ⁺ , Cl ⁻	H ^{+I} Cl ^{-I}
H ₂ O	H-O-H	2 H ⁺ , O ²⁻	H ^{+I} O ^{-II}
CO ₂	O=C=O	C ⁴⁺ , 2 O ²⁻	C ^{+IV} O ^{-II}

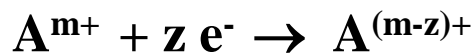
14.2 Oxidation and Reduction

Oxidation = Electron donation, i.e. increase of Oxidation Number



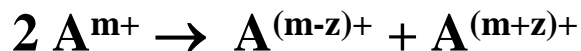
“Corrosion of iron“

Reduction = Electron Up Take, i.e. Decrease of Oxidation Number



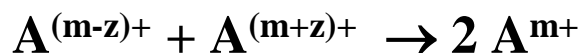
“Silver mirror reaction“

Disproportionation



⇒ Instability of Cu^{+}

Comproportionation



⇒ Formation of MnO_2

14.2 Oxidation and Reduction

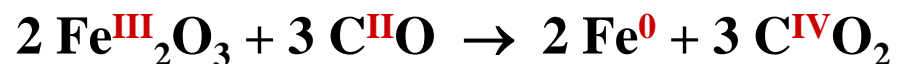
Redox Reactions are reversible

Oxidation of iron to Fe₂O₃

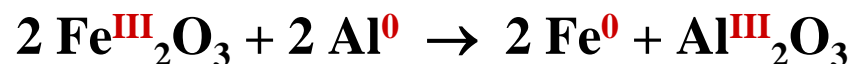


Reduction of Fe₂O₃ to iron Fe

a) Blast furnace process



b) Thermite-Reaction (welding of railroads)



14.2 Oxidation and Reduction

Excursus: Lunar Caustic (AgNO_3)

Ag^+ ($\text{Ag}^{\text{I}}\text{NO}_3$, $\text{Ag}_2^{\text{I}}\text{SO}_4$) is a strong oxidizing agent and can thus oxidize organic matter, being reduced to Ag^0 along the way

Application

- Removal of warts
- Disinfection
- Removal of proliferating tissue



14.3 Set Up of Redox Equations

To establish a Redox Reaction two Redox Systems are always needed

⇒ Separated Formulation of both Redox Systems

General approach

1. Set up of reaction equations of both redox systems
2. Electron balancing by determination of the least common multiple (lcm)
3. Charge compensation, i.e. establishing of electroneutrality
4. Mass balance, i.e. equal number of atoms of every kind on both sides of the redox equation

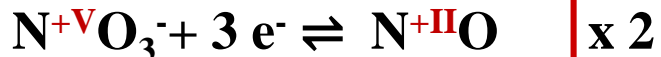
Example:



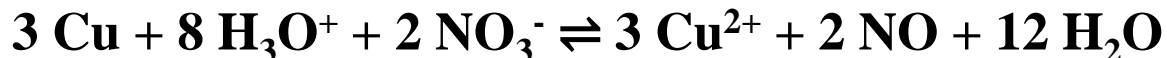
Redox system 1:



Redox system 2:



Redox equation:



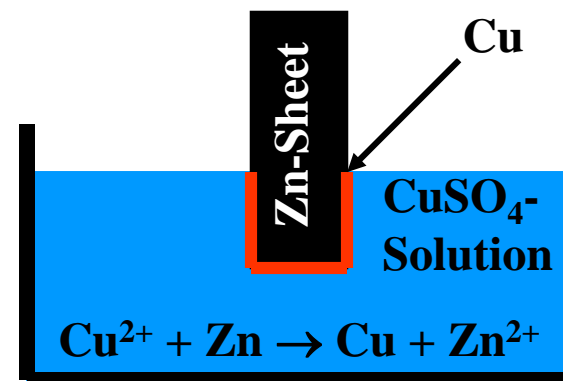
14.4 Galvanic Elements

The Working Principle of Galvanic Elements is based on different Tendencies of Chemical Species to take up or release Electrons

	<u>Reduced Form</u>		<u>Oxidized Form</u>	
Increasing tendency to release electrons ↑	Na	⇌	Na ⁺	+ e ⁻
	Zn	⇌	Zn ²⁺	+ 2 e ⁻
	Fe	⇌	Fe ²⁺	+ 2 e ⁻
	H ₂ + 2 H ₂ O	⇌	2 H ₃ O ⁺	+ 2 e ⁻
	Cu	⇌	Cu ²⁺	+ 2 e ⁻
	2 I ⁻	⇌	I ₂	+ 2 e ⁻
	Fe ²⁺	⇌	Fe ³⁺	+ e ⁻
	2 Cl ⁻	⇌	Cl ₂	+ 2 e ⁻
			Increasing tendency to take up electrons ↓	

Examples

1. Precipitation of Ag on a copper coin
2. Precipitation of Cu on a zinc sheet →

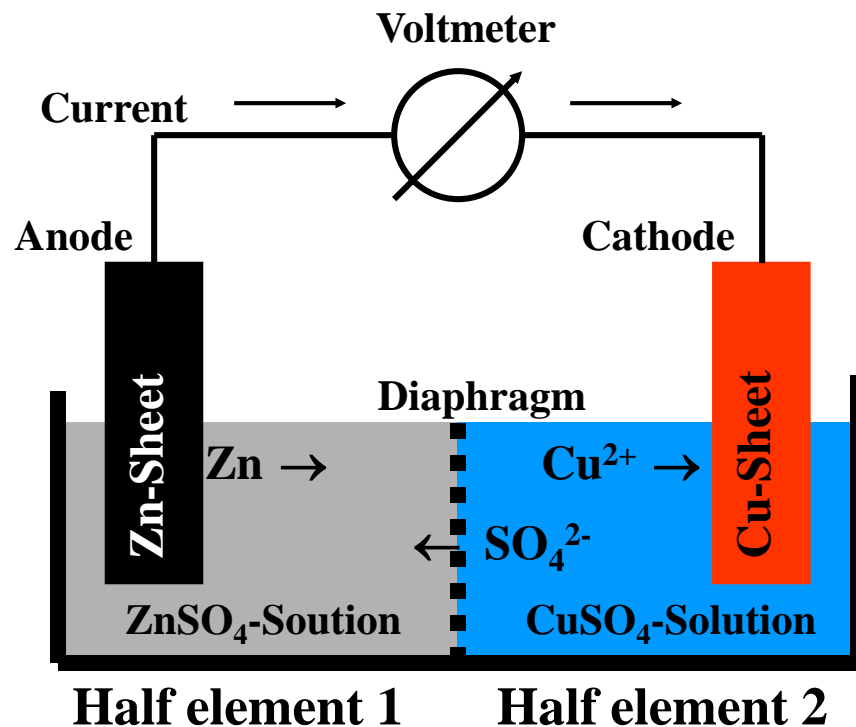


14.4 Galvanic Elements

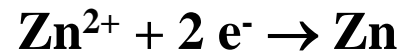
In a Galvanic Element, Oxidation and Reduction are spatially separated by a Diaphragm made of a porous Material

Daniell-Element

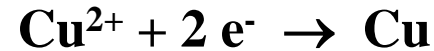
Example: $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$



Redox pair 1 (Half element 1)



Redox pair 2 (Half element 2)



Current running from the anode (Zn) to the cathode (Cu) equals the number of electrons transferred in the redox reaction. The total potential is given by the difference of the redox potentials $\Delta E = E_{\text{Cu}} - E_{\text{Zn}}$ (electromotive force)

14.5 Calculation of Redox Potentials

The Redox Potential E is described by Nernst's Equation

$$E = E^0 + \frac{R \cdot T}{z \cdot F} \ln \frac{c_{\text{Ox}}}{c_{\text{Red}}}$$

\Rightarrow Redox potential E for the reaction:



with

E^0 = Standard (Normal) potential

R = Gas constant = 8.314 J/Kmol

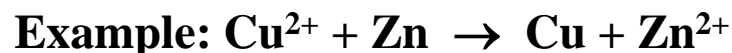
T = Temperature

F = Faraday-constant = 96487 As/mol

z = Number of transferred electrons

For T = 293 K and $\ln x = (\ln 10) \cdot \lg x$

$$E = E^0 + \frac{0.059}{z} \lg \frac{c_{\text{Ox}}}{c_{\text{Red}}} [\text{V}]$$

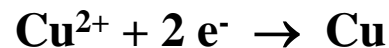


Redox pair 1 (Half element 1)



$$E_{\text{Zn}} = E^0_{\text{Zn}} + 0.059/2 \cdot \lg c_{\text{Zn}^{2+}}$$

Redox pair 2 (Half element 2)



$$E_{\text{Cu}} = E^0_{\text{Cu}} + 0.059/2 \cdot \lg c_{\text{Cu}^{2+}}$$

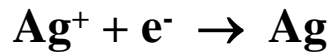
Total potential

$$\Delta E = E_{\text{Cu}} - E_{\text{Zn}} = E^0_{\text{Cu}} - E^0_{\text{Zn}} + 0.059/2 \cdot \lg (c_{\text{Cu}^{2+}}/c_{\text{Zn}^{2+}})$$

14.5 Calculation of Redox Potentials

Due to the Dependence of the Redox Potential on the Ionic Concentration / Activity, a Galvanic Element can be built via a concentration Chain

Reaction of half element 1



$$E_{\text{Ag}(1)} = E^0_{\text{Ag}} + 0.059 \cdot \lg c_{\text{Ag}^+(1)}$$

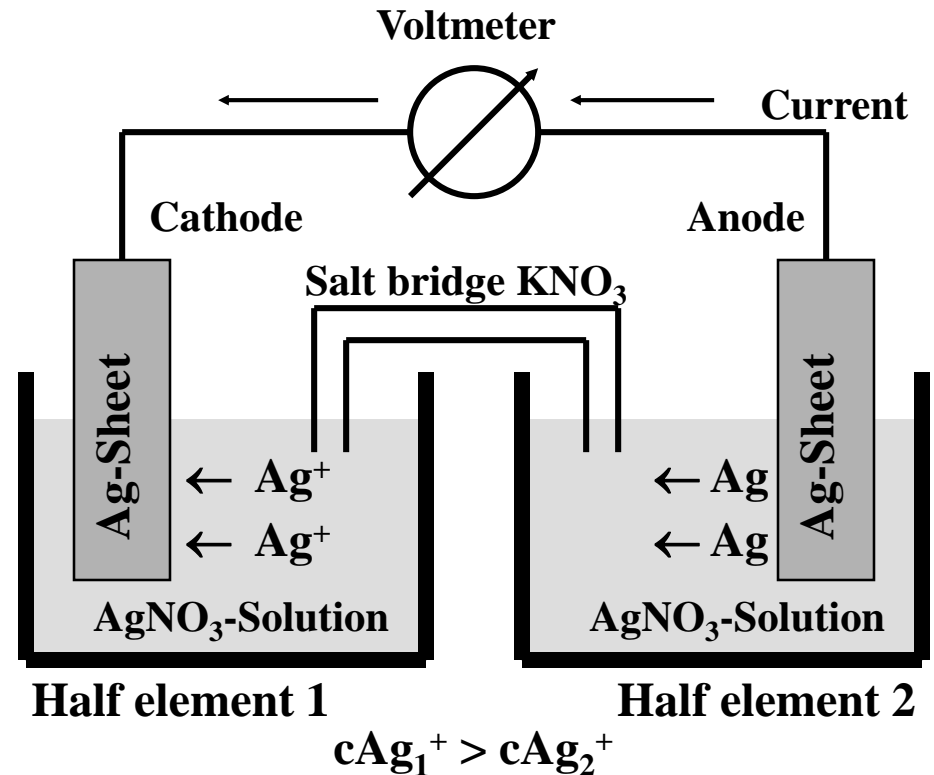
Reaction of half element 2



$$E_{\text{Ag}(2)} = E^0_{\text{Ag}} + 0.059 \cdot \lg c_{\text{Ag}^+(2)}$$

Total potential

$$\Delta E = E_{\text{Ag}(1)} - E_{\text{Ag}(2)} = 0.059 \cdot \lg(c_{\text{Ag}^+(1)} / c_{\text{Ag}^+(2)})$$



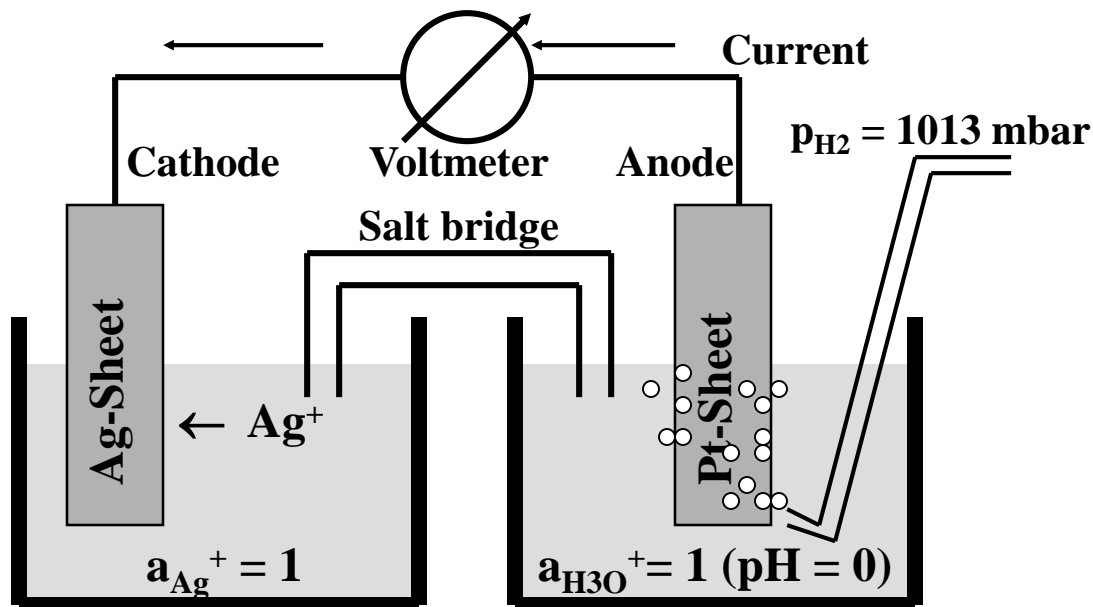
14.6 Standard Hydrogen Electrode

The Potential of a Single Redox Pair cannot be measured Directly, because it is only possible to determine the Total Voltage of a Galvanic Element

⇒ Choice of reference electrode ⇒ standard hydrogen electrode with $E^0_{\text{H}} = 0.0 \text{ V}$

Redox system: $\text{H}_2 + 2 \text{H}_2\text{O} \rightleftharpoons 2 \text{H}_3\text{O}^+ + 2 \text{e}^-$

Redox potential: $E_{\text{H}} = E^0_{\text{H}} + 0.059/2 \cdot \lg(a^2_{\text{H}_3\text{O}^+}/p_{\text{H}_2})$



Standard silver electrode

Standard hydrogen electrode

for $a_{\text{H}_3\text{O}^+} = 1$ and $p_{\text{H}_2} = 1 \text{ bar}$:
 $E_{\text{H}} = E^0_{\text{H}} = 0.0 \text{ V}$

$$\Delta E = E_{\text{Ag}} - E_{\text{H}}$$

$$\Delta E = E^0_{\text{Ag}} + 0.059 \cdot \lg a_{\text{Ag}^+}$$

for $a_{\text{Ag}^+} = 1$

$$\Delta E = E^0_{\text{Ag}} = + 0.80 \text{ V}$$

14.7 Electrochemical Voltage Series

Redox Potentials of all Redox Systems refer to the Standard Hydrogen Electrode. Sorted according to increasing Potential one obtains the Electrochemical Series

Reduced form	\rightleftharpoons	Oxidized form	+ z e ⁻	Standard potential E ⁰ [V]
Li	\rightleftharpoons	Li ⁺	+ e ⁻	-3.04
K	\rightleftharpoons	K ⁺	+ e ⁻	-2.92
Na	\rightleftharpoons	Na ⁺	+ e ⁻	-2.71
Zn	\rightleftharpoons	Zn ²⁺	+ 2 e ⁻	-0.76
Fe	\rightleftharpoons	Fe ²⁺	+ 2 e ⁻	-0.41
Sn	\rightleftharpoons	Sn ²⁺	+ 2 e ⁻	-0.14
H ₂ + 2 H ₂ O	\rightleftharpoons	2 H ₃ O ⁺	+ 2 e ⁻	0.0
Cu	\rightleftharpoons	Cu ²⁺	+ 2 e ⁻	0.34
2 I ⁻	\rightleftharpoons	I ₂	+ 2 e ⁻	0.54
Fe ²⁺	\rightleftharpoons	Fe ³⁺	+ e ⁻	0.77
Ag	\rightleftharpoons	Ag ⁺	+ e ⁻	0.80
Hg	\rightleftharpoons	Hg ²⁺	+ e ⁻	0.85
Au	\rightleftharpoons	Au ³⁺	+ 3 e ⁻	1.50
2 F ⁻	\rightleftharpoons	F ₂	+ 2 e ⁻	2.87

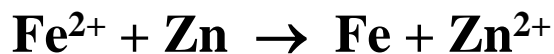
Increasing reductive
strength ↑
↓
Increasing oxidizing

14.7 Electrochemical Voltage Series

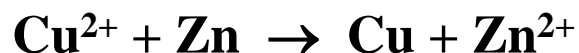
The Voltage Series is a Tool to predict which Redox Reactions are possible. The Reduced Form of a Redox System only transfers Electrons to the Oxidized Form of such a Redox System that is located in the Voltage Series below

Reduced form	\rightleftharpoons	Oxidized form	+ z e ⁻	Standard potential E ⁰ [V]
Zn	\rightleftharpoons	Zn ²⁺	+ 2 e ⁻	-0.76
Fe	\rightleftharpoons	Fe ²⁺	+ 2 e ⁻	-0.41
Cu	\rightleftharpoons	Cu ²⁺	+ 2 e ⁻	+0.34

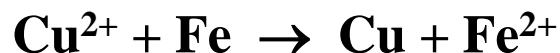
The following reactions are thus possible:



$$\Delta E = E^0_{\text{Fe}} - E^0_{\text{Zn}} = +0.35 \text{ V}$$



$$\Delta E = E^0_{\text{Cu}} - E^0_{\text{Zn}} = +1.10 \text{ V}$$



$$\Delta E = E^0_{\text{Cu}} - E^0_{\text{Fe}} = +0.75 \text{ V}$$

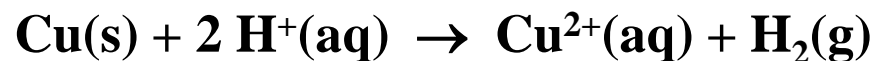
(Potentials valid for $c_{\text{Me}1} = c_{\text{Me}2}$)

14.7 Electrochemical Voltage Series

The Electromotive Force ΔE (EMF) is linked to the free Standard-Reaction-Enthalpy ΔG^0

$$\Delta G^0 = -z \cdot F \cdot \Delta E^0$$

Example



$$\Delta E^0 = E^0_{\text{H}} - E^0_{\text{Cu}} = 0.0 - 0.34 = -0.34 \text{ V}$$

$$\Delta G^0 = -2 \cdot 96500 \text{ As/mol} \cdot 0.34 \text{ V}$$

$$= 65610 \text{ AVs/mol}$$

$$= 65610 \text{ Ws/mol}$$

$$= 65.610 \text{ kJ/mol}$$

\Rightarrow strongly positive standard-reaction enthalpy

\Rightarrow reaction does not run voluntarily!

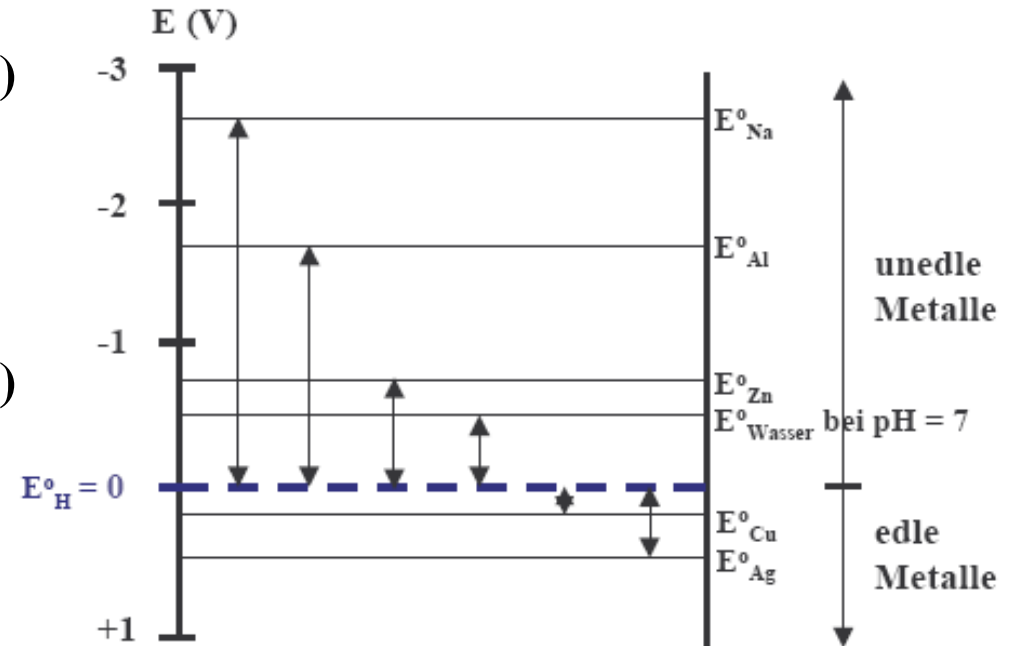
14.7 Electrochemical Voltage Series

The Redox Potential of many Redox Reactions depends on the pH-Value

Example: Reaction of metals with acids and water

$$\begin{aligned}\text{pH} = 0: E_{\text{H}} &= E_{\text{H}}^0 + 0.059/2 \cdot \lg(a_{\text{H}_3\text{O}^+}^2/p_{\text{H}_2}) \\ &= E_{\text{H}}^0 + 0.0 \\ &= 0.0 \text{ V}\end{aligned}$$

$$\begin{aligned}\text{pH} = 7: E_{\text{H}} &= E_{\text{H}}^0 + 0.059/2 \cdot \lg(a_{\text{H}_3\text{O}^+}^2/p_{\text{H}_2}) \\ &= E_{\text{H}}^0 + 0.059/2 \cdot \lg 10^{-14} \\ &= -0.41 \text{ V}\end{aligned}$$



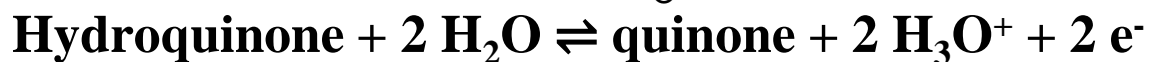
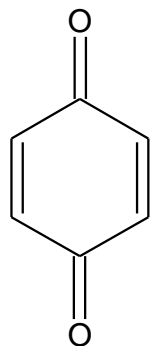
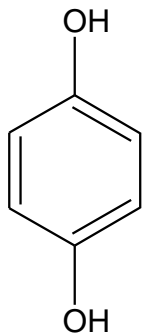
In general: $E_{\text{H}} = 0.059/2 \cdot \lg[\text{H}_3\text{O}^+]^2 = -0.059 \cdot \text{pH}$

\Rightarrow The pH-value can be determined electrochemically

\Rightarrow Measurement via pH-electrode

14.7 Electrochemical Voltage Series

The pH Dependence Redox System Quinone/Hydroquinone



$$E^0 = - 0.70 \text{ V}$$

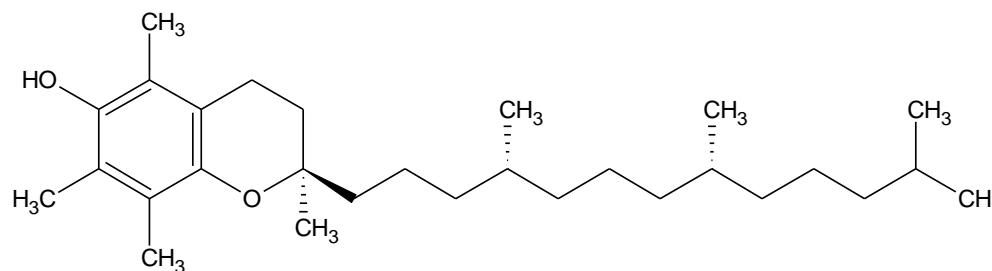
$$E = E^0 + \frac{0.059}{z} \lg \frac{[\text{quinone}][\text{H}_3\text{O}^+]^2}{[\text{hydroquinone}]} = E^0 + \frac{0.059}{z} \lg \frac{[\text{quinone}]}{[\text{hydroquinone}]} - 0.059 \times \text{pH}$$

Biochemically important quinone/hydroquinone-systems

Plastoquinone

Ubiquinone (coenzyme Q)

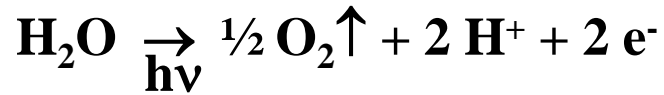
Tocopherole (vitamin E) →



⇒ Electron transport in photo synthesis and respiratory chain

14.7 Excursus: Light Reactions in Photosynthesis

The Biochemical Energy Carrier ATP is formed by an electrochemical Gradient



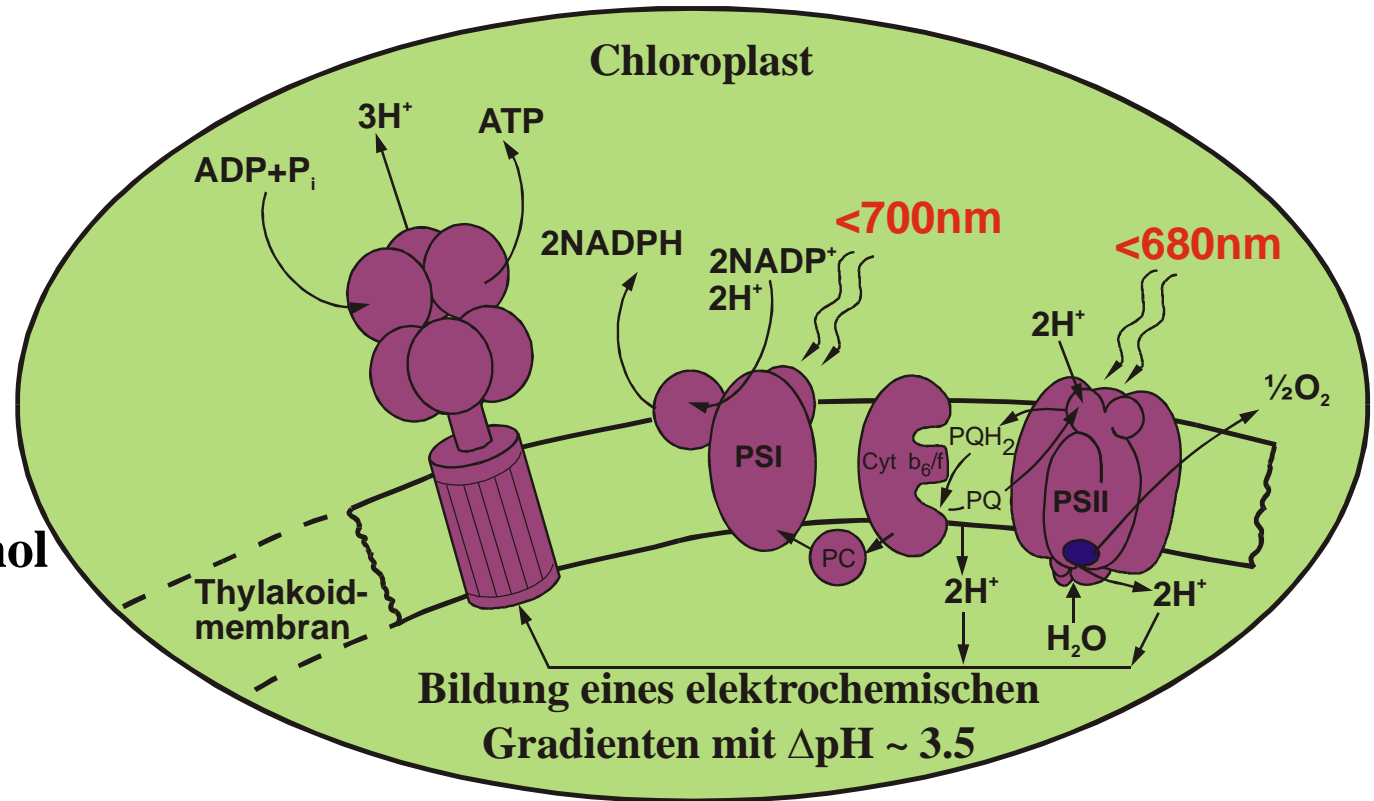
$$\Delta\text{pH} \sim 3.5$$

$$\begin{aligned} \Delta E &= E_1 - E_2 \\ &= 0.059/z \cdot \log(c_1/c_2) \\ &= 0.059 \cdot \Delta\text{pH} \\ &= 0.2 \text{ V} \end{aligned}$$

$$\Delta G = -n \cdot F \cdot \Delta E = 20 \text{ kJ/mol}$$



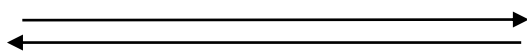
$$\Delta G = 30.5 \text{ kJ/mol}$$



14.8 Electrolysis

Redox Reactions that do not proceed voluntarily can be forced by electrical Work

Example

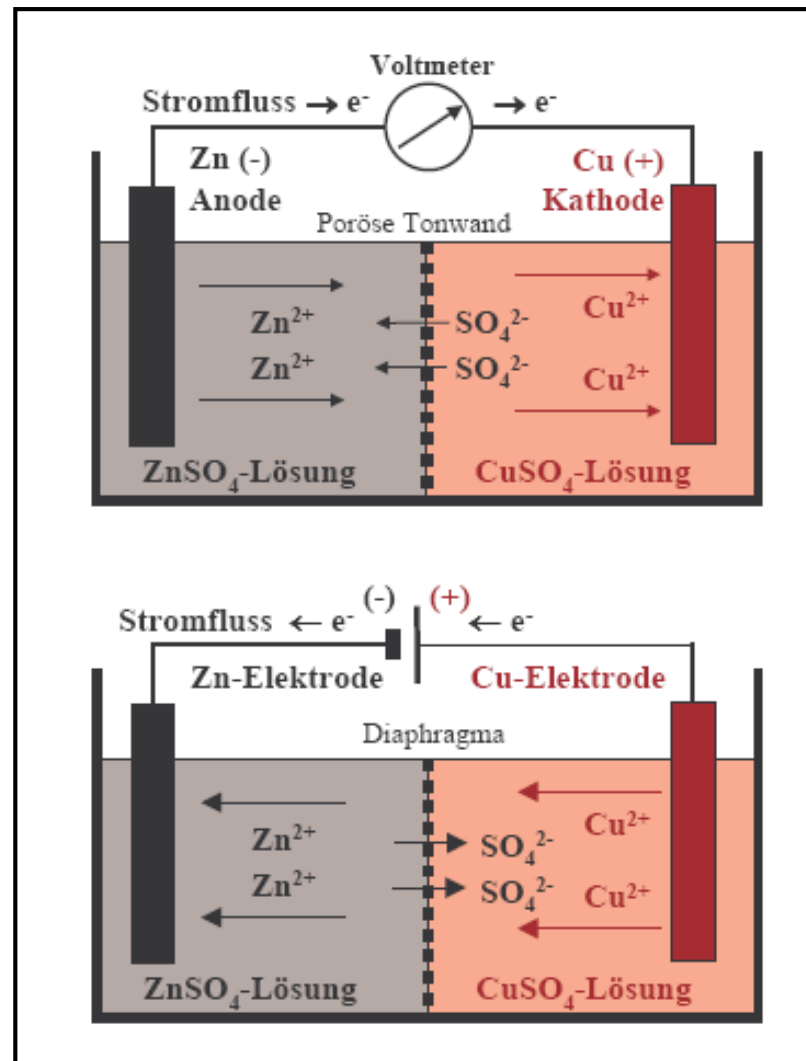


forced (electrolysis)

For an electrolysis a direct voltage U is applied

U = dissociation voltage ΔE + overvoltage

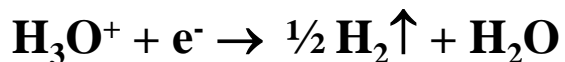
The overvoltage is needed due to the kinetic inhibition of the product formation at the electrodes



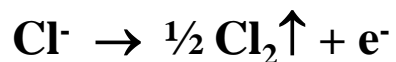
14.8 Electrolysis

Electrolysis of Hydrochloric Acid

Cathode reaction



Anode reaction



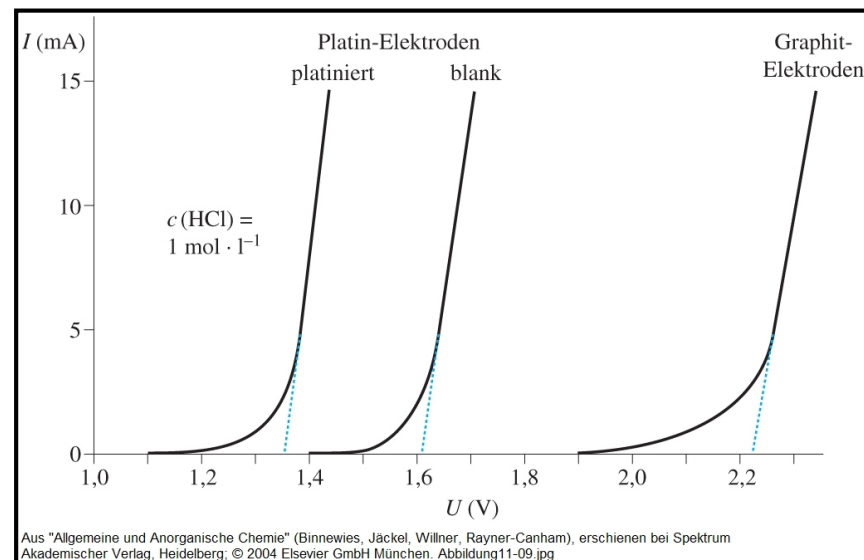
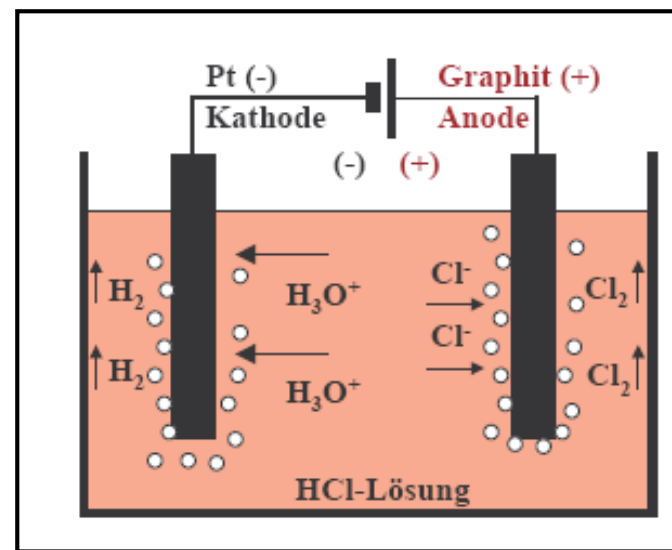
Total reaction



$$\Delta E = E^0_{1/2\text{Cl}_2/\text{Cl}^-} - E^0_{\text{H}^+/\frac{1}{2}\text{H}_2} = +1.36 \text{ V}$$

The overvoltage depends on many factors:

- Electrode material
- Current density
- Temperature
- Precipitated matter
- ...



14.9 Galvanic Voltage Sources

Galvanic Elements are energy Transformers in which Chemical Energy is directly converted into electrical Energy

Primary elements

irreversible

Secondary elements (accumulators)

reversible

Fuel cells

irreversible

Primary elements ⇒

Negative pole

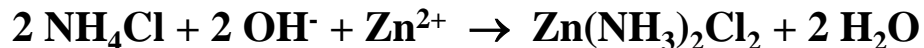


Positive pole

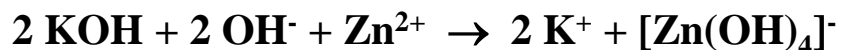


Electrolyte

Zinc-graphite-battery (Leclanche-element)

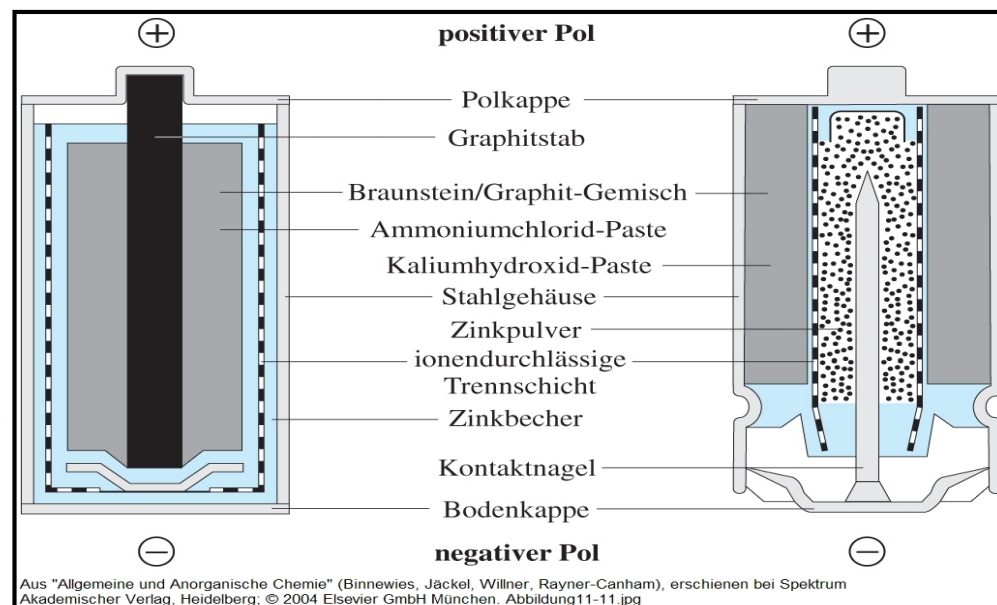


Alkali-manganese-battery



Zinc-graphite-battery

Alkali-manganese-battery



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14.9 Galvanic Voltage Sources

Secondary Elements

1. Ni-Cd-accumulator



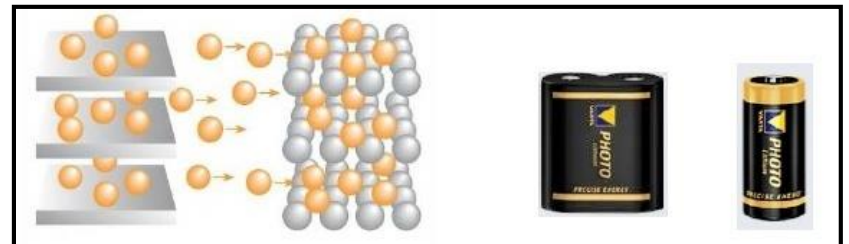
2. Pb-accumulator



3. Lithium-ion-accumulator



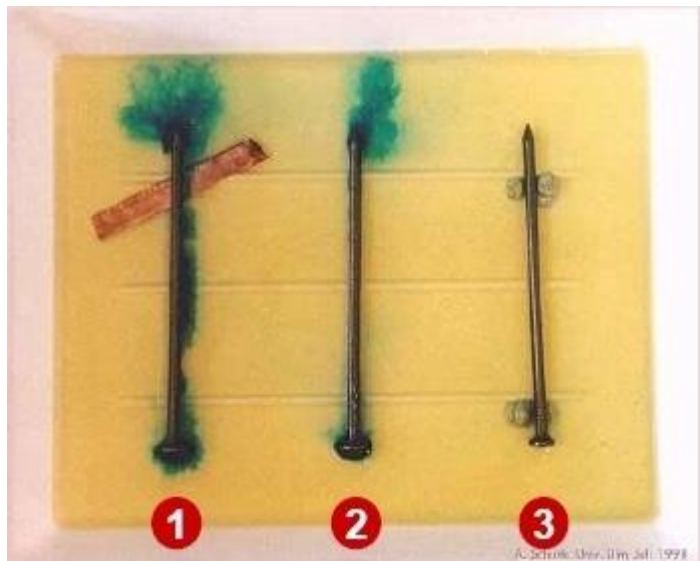
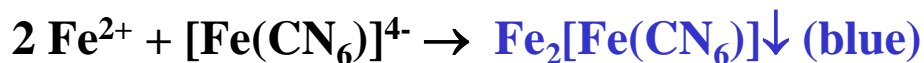
⇒ Intercalation of Li in graphite layers



14.10 Corrosion and Corrosion Inhibition

Corrosion, i.e. Oxidation of precious Metals can be accelerated or inhibited by local Elements

Corrosion of iron in a sodium chloride solution can be made visible by $K_4[Fe(CN_6)]$:

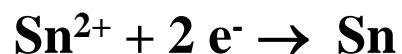


Parts made from iron can be protected from corrosion by connecting them with less noble metals (Zn, Mg, ...) as sacrificial anode \Rightarrow bridges, pipelines, fuel tanks etc.

14.10 Corrosion and Corrosion Inhibition

Local Elements do also form upon Contact of Amalgam with Gold Fillings

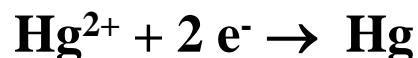
Metals in amalgam: Sn, Cu, Ag, Hg



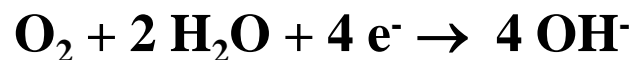
$$E^0_{\text{Sn}} = -0.14 \text{ V}$$



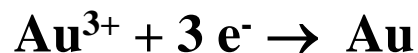
$$E^0_{\text{Cu}} = +0.34 \text{ V}$$



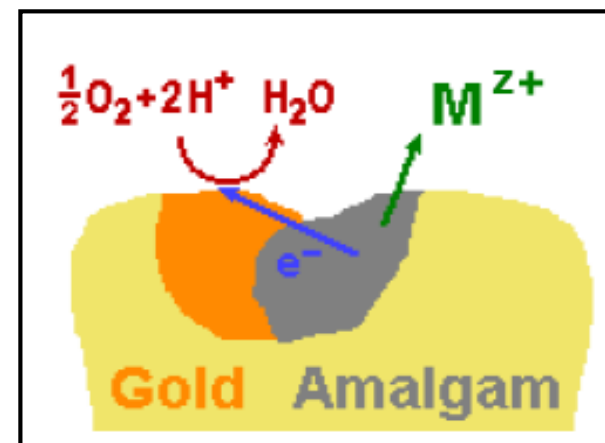
$$E^0_{\text{Hg}} = +0.85 \text{ V}$$



$$E^0_{\text{O}_2/\text{OH}^{-}} = +1.24 \text{ V}$$



$$E^0_{\text{Au}} = +1.50 \text{ V}$$



Through the formation of the local element the the less noble metals are prone to dissolution into the saliva.

It must thus be ensured that amalgam and gold fillings never come into contact with one another.