Chemistry I

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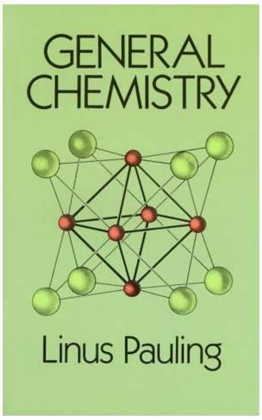
1. Introduction



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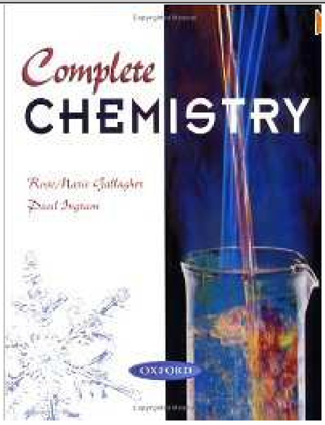

basic
336 Pages; € 25.-
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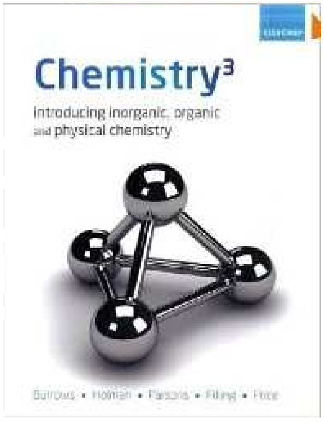

advanced
1397 Pages; € 53.-
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On-line

Introduction to Chemistry (Mark Bishop)
http://preparatorychemistry.com/

On-line textook (R. Dickerson; CalTech)
http://caltechbook.library.caltech.edu/178/

On-line lectures and notes (MIT):
http://ocw.mit.edu/courses/chemistry/

Test your knowledge on:
http://www.chemistry-drills.com/

History I:
Unintentional Chemistry

3000 BC.: Smelting of lead, copper and tin (bronze)

1. Roasting of metal ore at about 300°C :

Malachite: $CuCO_3 \longrightarrow CuO + CO_2$

2. Reduction at >1000°C: $2\ CuO + C \longrightarrow 2\ Cu + CO_2$
metal oxide + charcoal
→ metal + carbon dioxide

History II:
Alchemy

Intentional, traditional, non-scientific chemistry;
Protoscience: Precursor of modern chemistry:

- *Creation of the "philosopher's stone," (catalyst?)⇒*
- *Conversion of base metals into solver or gold*
- *Search for the universal solvent "alkahest"*

Notion of elements:

Greece	**Buddhism**	**China (Tao)**
Fire (hot)	Fire	Fire
Water (wet)	Water	Water
Earth (dry)	Earth	Earth
Air (cold)	Wind	
Spirit/Ether	Space	
		Wood
		Metal

Some Discoveries/Inventions:

- Sal ammoniac (NH_4Cl), cinnabar (HgS):
  by Abu Musa Jabir ibn Hayyan, Arabia 8. Jh.
- Alcohol (ethanol C_2H_5OH), Italy ~1100 from wine
- Medicals; mercury, arsenic, antimony comp:
  by Paracelsus, 16. Jh.
- Phosphorous: Hennig Brand; Hamburg 1669
- Porcelain: Johann Friedrich Böttger 1707/08

Discovery of Phosphor
by Hennig Brand (1669)

History III
Chemistry as Natural Science

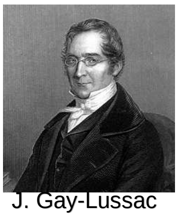
After 17. Jh.:
Scientific chemistry:
Exemption from dogma and religion.
Rational conclusions
based of observation
and experiments.

Robert Boyle (1627-1691)
Irish researcher
"The Sceptical Chymist" (1661)

Joseph Priestley
(1733-1804)
Engl. researcher
Invent.: NH_3,
N_2O, CO, SO_2

Carl W. Scheele
(1742-1786)
Swed. Pharm.
O_2, Cl_2, Ba, Mn;
HCN, lactic acid

Antoine Lavoisier
(1743-1794)
French Chem.
Oxidation



J. Gay-Lussac
(1778-1850)
French Chem.
Ideal gas law

Justus v. Liebig
(1803-1873)
German Chem.
Chem.Analysis

Difference Chemistry-Physics

Physics: (Change of) State of Matter

Chemistry: Change of Composition of Matter

Example:
Iron: metallic, shiny, conductive, malleable.

Heating iron ⇒ melting
cooling ⇒ solidification.
Properties unchanged.
Reversible change of state

Iron in humid air ⇒ gets rusty
Rust: red-brown, non-conductive
not moldable
⇒ Change of matter

Another example:

Platinum wire heating to red-hot
Cooling: No change in prop.
Emission of light: physical proc.

Heating magnesium⇒
combustion with light emission⇒
magnesium oxide (white powder)
⇒ change of matter

Last Example:

Heavy cooling of air ⇒ liquefaction
Slow warming up (distillation) ⇒
Separation of oxygen and nitrogen
Properties unchanged.

Respired oxygen converts
carbohydrates into CO_2+H_2O.
Energy is released.
⇒ Chemical process.

Liquefaction, evaporation, melting,
distillation: physical processes

Combustion, oxidation,
chem. synthesis: Chemical proc.

Beginning and Resources of Chemical Industry

before 1820: Production of:
- Soda (sodium carbonate) for processing of glass, bleaching agents, detergents, etc.
- Synthetic fertilizers
- Dyes

Resources of chemical industry before 1870:
- Coal
- Minerals
- Plant products
- Animal products

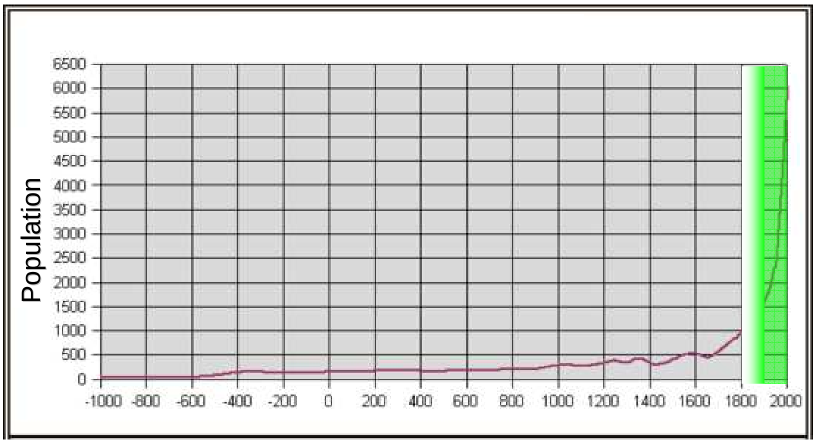
Resources of chemical industry after 1870 - ?
- Crude oil

Chemical Hazards

21. Sept. 1921; BASF, Oppau, : Explosion of fertilizer plant:
561 Dead, 2000 Injured, 900 apartments destroyed, 100 m crater

$$2\ NH_4NO_3 \rightarrow 4\ H_2O + 2\ N_2 + O_2$$

Benefit from Chemical Industry Demographics

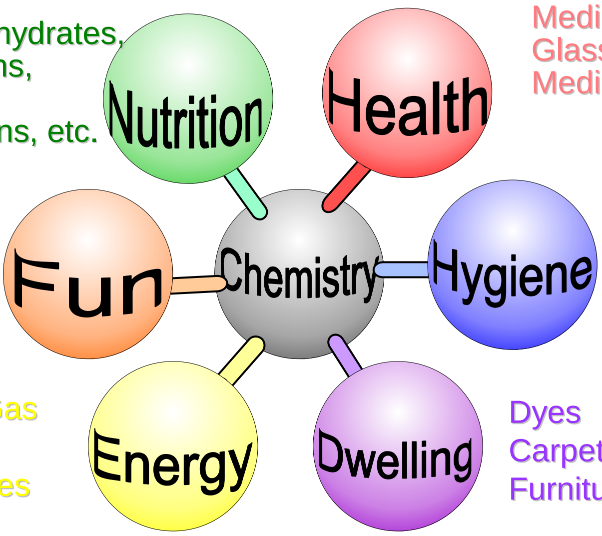


Development of chemical industry

- Synth. fertilizer
- Pesticides
- Medicals
- Hygiene items

Why bother with Chemistry?

Chemistry affects our life's:



Carbohydrates,
Proteins,
Fats,
Vitamins, etc.

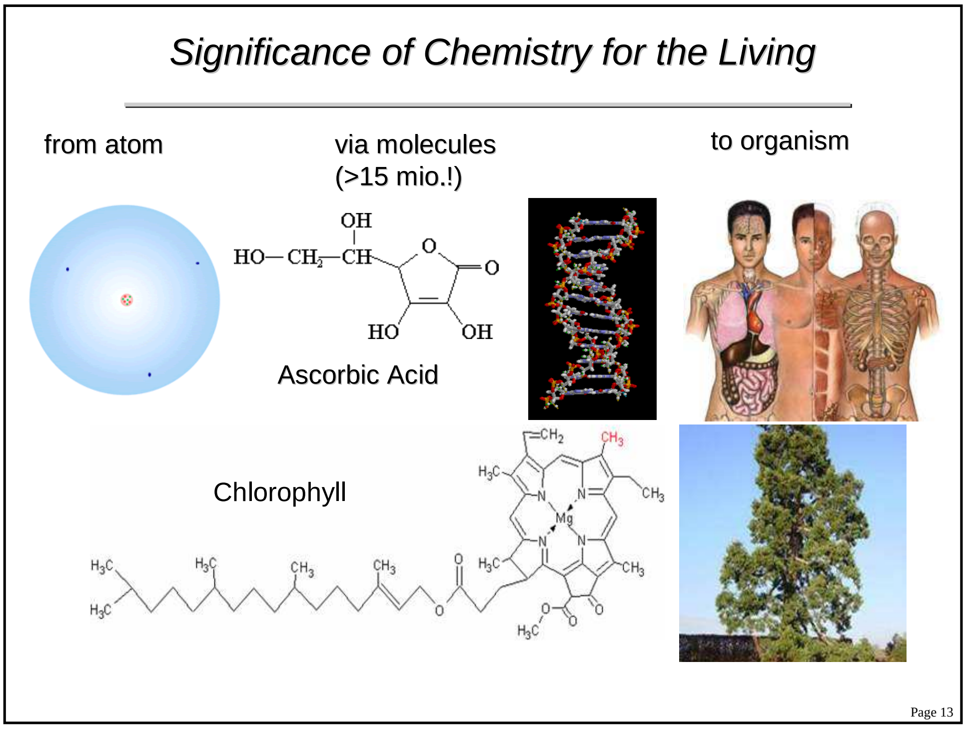
Medicine
Glasses
Medical devices

Toy
Sports equipment
Mobiles

Detergents
Soap
Tooth paste

Coal/Gas
Petrol
Batteries

Dyes
Carpets
Furniture



Significance of Chemistry for the Living

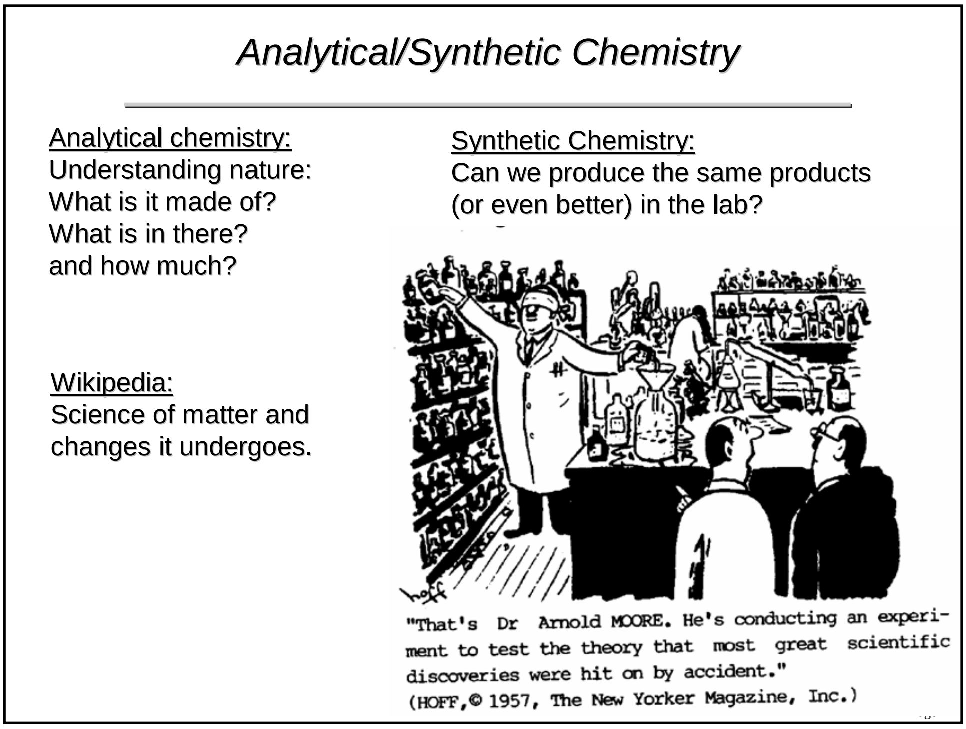
from atom

via molecules
(>15 mio.!)

to organism

Ascorbic Acid

Chlorophyll



Analytical/Synthetic Chemistry

Analytical chemistry:
Understanding nature:
What is it made of?
What is in there?
and how much?

Synthetic Chemistry:
Can we produce the same products
(or even better) in the lab?

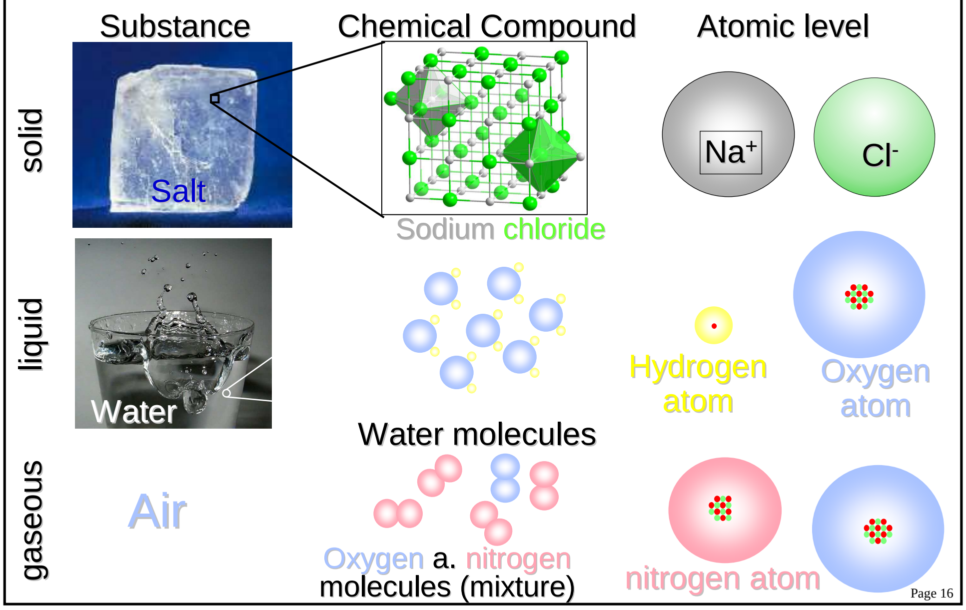
Wikipedia:
Science of matter and
changes it undergoes.

"That's Dr Arnold MOORE. He's conducting an experiment to test the theory that most great scientific discoveries were hit on by accident."
(HOFF,© 1957, The New Yorker Magazine, Inc.)

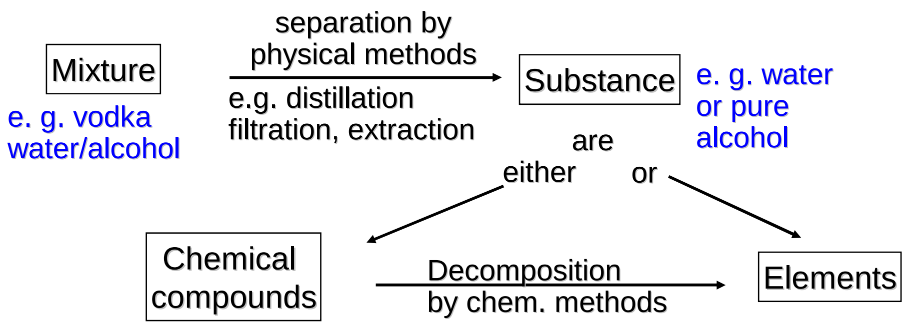
Basic Terms and Concepts
Measures and Units (SI)

Measure	Symbol	Unit	Symbol
Length	l	Meter	m
Mass	m	Gramm	g
Volume	V	Liter	L
Density	ρ	Gramm per cm^3	g/cm^3
Temperature	T	Kelvin	K
Force	F	Newton	$N = kg{\cdot}m/s^2$
Pressure	p	Pascal	$Pa = N/m^2$
Energy	E	Joule	$J = kg{\cdot}m^2/s^2$
Amount of substance	n	Mole	mol
Molar Mass	M	Mass per Mole; $M = m/n$	g/mol
Molar concentration	c	Mole per volume; $c=n/V$	mol/l
Molar Enthalpy	H	Joule per Mol	J/mol
Molar Entropy	S		J/mol·K

General Structure of Matter



Mixtures, Substances, Compounds, Elements



Mixture

e. g. vodka
water/alcohol

separation by
physical methods

e.g. distillation
filtration, extraction

Substance

e. g. water
or pure
alcohol

are
either or

Chemical
compounds

Decomposition
by chem. methods

Elements

composed of two or more different
chemical elements (types of atoms)
connected by chemical bonds

e. g. water H_2O
two atoms of hydrogen (H)
one atom of oxigen (O)

one type oft atom;
no decomposition
by chem. methods

e. g. hydrogen (H)
oxygen (O)
iron (Fe)

Symbols of Chemical Element

Symbols used for abbreviation of chemical elements by *Berzelius; today by IUPAC*:
One- or two-letters long, only first capitalized.
Mostly derived from Greek or Latin words.

Jöns Jakob Berzelius
Swedish chemist
(1779-1848)

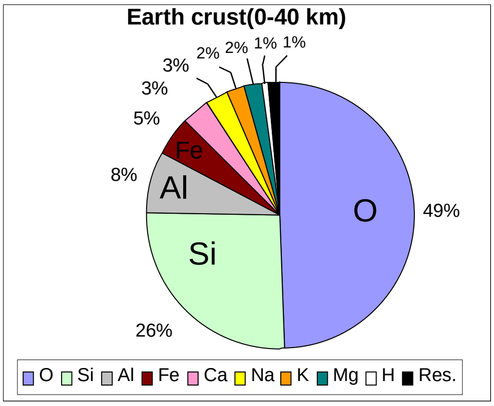
H	Hydrogen
He	Helium
Li	Lithium
Be	Beryllium
B	Boron
C	Carbon
N	Nitrogen
O	Oxygen
F	Fluorine
Ne	Neon

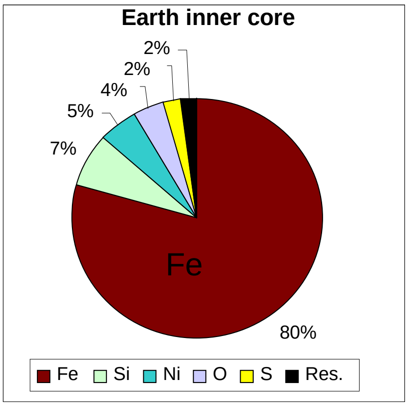
Na	Sodium
Mg	Magnesium
Al	Aluminum
Si	Silicon
P	Phosphorus
S	Sulfur
Cl	Chlorine
Ar	Argon
K	Potassium
Ca	Calcium

First 20 elements

Natural Abundance of Elements

Over 90% of the universe is hydrogen (H);
second most is helium (He).





Common compounds:
SiO_2, Silicates, Al-, iron oxides, carbonates, sulfates, hydroxides

Earth inner core (3000 km) mainly composed of iron (2900°C, liquid). Fe/Ni-convection at mantle ⇒magnetism

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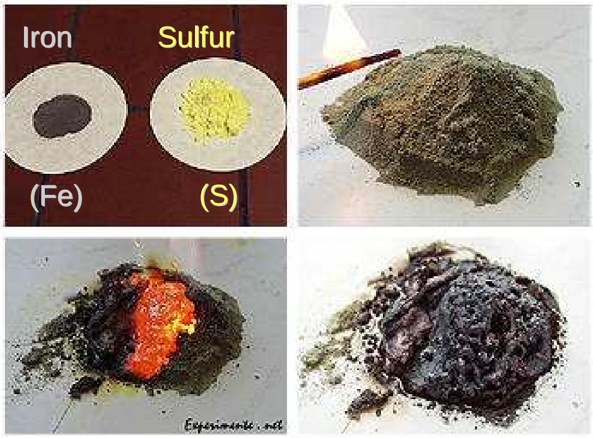
Change of Matter by Chemical Reaction



Iron-Sulfur-
Mixture: Fe + S

How can it be separated?

Iron-sulfur-compound
Iron sulfide (FeS)

No physical separation into iron and sulfur possible

Chemical reaction

Chemical Reaction

A chemical reaction is a process that leads to the transformation of one set of chemical substances (reactants; reagents) to another (products).

Chemical equations used to graphically illustrate chemical reactions:

$\boxed{\text{Reactant 1 (+ reactant 2)} \longrightarrow \text{product 1 + (product 2)}}$

A chemical reaction alters the combination of atoms in substances, the number of atoms of each elements remains constant.

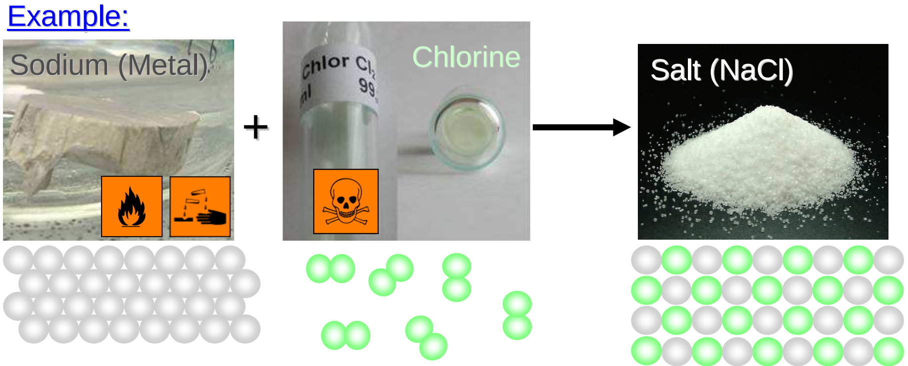
"The mass of matter remains constant during chemical reactions".

(Law of Conservation of Mass)

Antoine Lavoisier
fr. Chem. (1743-1794)

Chemical Reaction
Example: Sodium Chloride

Example:

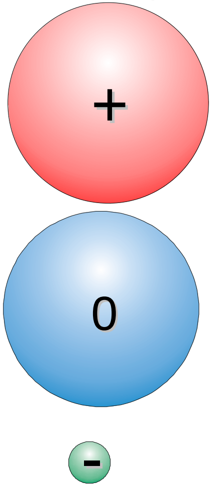


Chemical reactions involve a *"rearrangement"* of atoms. New compounds are formed with different properties.

Which substance can react with which other substance yielding which compound in which molar ratio?

Elemental Particles

Matter composed of atoms, composed of three elemental particles:



Proton (p^+): "big", "heavy" (relatively!), positive
mass ~ 1 u

Neutron (n): "big", "heavy" (relatively!), neutral
mass ~ 1 u

Electron (e^-): tiny, lightweight, negative
mass ~ 1/1800 u

u extremely small unit: 1 u = $1{,}66 \cdot 10^{-27}$ Kg

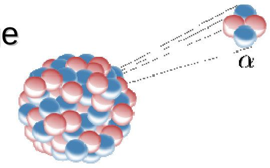
Radiation

Radiation is a process in which waves or particles travel through a medium or space ⇒ Transport of energy or mass.
Dualism: Each radiation has wave *and* particle character.

Electromagnetic waves (light, micro-, radio-, x-ray)
Energy ~ frequency ~1/wave length

Radioactive decay:
Atomic nucleus emits particle or wave

Name	Character	Mass	Charge
α-radiation	He nucleus: 2 P^+; 2 N	4 u	+2
β-radiation	Electron	1/1823 u	-1
γ-radiation	electromag. wave	-	-



2. General Chemistry
Atomic Structure: Early Atomic Models

Law of defined proportions = const. composition (J. Proust, 1794):
"A chemical compound always contains exactly the same proportion of elements by mass". E. g. water: oxygen:hydrogen = 8:1

Law of multiple proportions (J. Dalton, 1803):
"The proportions of mass of two elements in *different* compounds are rations of small whole numbers". E.g.:
100 g of carbon reacts with 133 g oxygen to carbon monoxide
100 g of carbon reacts with 266 g oxygen to carbon dioxide
266:133=2:1

Stoichiometry

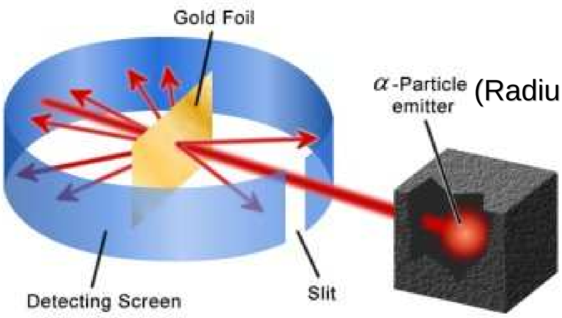
Daltons Atomic Theory (1808):

- Elements are made of tiny particles called atoms.
- The atoms of a given element are different from those of any other element; they can be distinguished by their respective relative atomic weights.
- All atoms of a given element are identical.
- Atoms of one element can combine with others to form chemical compounds; a given compound always has the same relative numbers of types of atoms.
- Atoms cannot be created, divided into smaller particles, nor destroyed; a chemical reaction simply changes the way atoms are grouped together.

Geiger-Marsden Gold Foil Experiment
Rutherford Model

1910: α-particles (***positive*** He-nuclei) directed onto very thin gold foil: Very few particles deflected ⇒

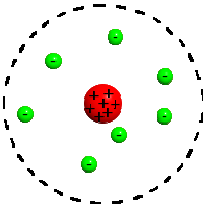
1. Atoms are almost "empty"
2. Atomic mass concentrated in positive nucleus
3. Atomic volume represented by negative shell



(Radium)

ZnS

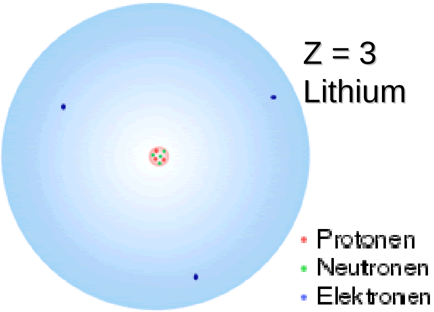
Sir E. Rutherford
New Zealand Chem.



Rutherford Model

Rutherford Atomic Model

Atoms have a **positive core (nucleus)**,
surrounded by **negative electron cloud (shell)**.



Z = 3
Lithium

Protons and neutrons located in nucleus (⇒nucleons).
Neutrons: no charge,
Protons: charge = +1 ⇒
Number of protons = number of (pos.) charges in nucleus
= Atomic number (Z) in periodic system of elements (PSE)

The number of protons determines the element

Atomic diameter ~ 10^{-10} m, nucleus only 1/100000 of it:

Nucleus: tiny, "heavy", positive   Shell: "bigger", light, negative

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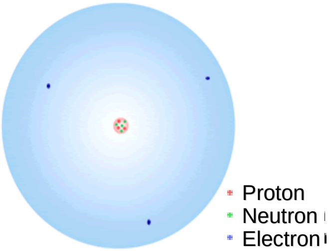
Atomic Mass

Number of nucleons (protons + neutrons)= atomic mass (m_a),
Mass of electrons can be neglected.

The number of protons determines, which element (type of atom) (= atomic number Z)

The number of neutrons N plus protons Z determines, which mass is has. (atomic mass m_a = Z + N)



Example: Lithium
3 protons ⇒ atomic number Z = 3
4 neutrons ⇒ atomic mass = 7

Molecular Mass

The mass of molecule m_M of a chemical compound is the sum of the atomic masses of the constituting elements

Example: Glucose $C_6H_{12}O_6$

The empirical formula indicates the number of atoms of each element in the molecule

$$m_M = 6 \cdot m_a(C) + 12 \cdot m_a(H) + 6 \cdot m_a(O)$$

$m_a(C) = 12$ u

$m_a(H) = 1$ u

$m_a(O) = 16$ u

$$m_M \text{ (Glucose)} = 6 \cdot 12u + 12 \cdot 1u + 6 \cdot 16u = \underline{180\ u}$$

Amount of Substance, Mole

The mass unit u measures extremely small quantities (single molecules): The **Amount of Substance *n*** (or Chemical Amount) with unit Mole is a quantity that measures the size of an ensemble of elementary entities (atoms, molecules other particles) on lab-scale.

The Amount of Substance is no mass, nor a number of entities - it is, however, closely related to both:

The Amount of Substance *n* is the mass *m* of a portion related to the Molar Mass *M* of the substance. The Molar Mass *M* is a substance-specific quantity with the unit [g/mol].

Examples:

Atomic/molecular mass	Molar Mass *M*
Li = 7 u	M(Li) = 7 g/mol
H_2O = 18 u	$M(H_2O)$ = 18 g/mol
H_2 = 2 u	$M(H_2)$ = 2 g/mol
$C_6H_{12}O_6$ = 180 u	$M(C_6H_{12}O_6)$ = 180 g/mol

One Mole Li weights 7 g, 1 Mole water ≈ 18 g; 2 Mol H_2O ≈ 36 g.

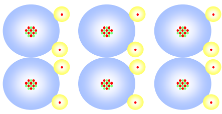
Avogadro´s Number
Illustration of the Mole

An amount of substance n = 1 mol contains always the same number of particles: Avogadro´s Number N_A:

$$1 \text{ mol} \approx N_A = 6{\cdot}10^{23} \text{ particles}$$

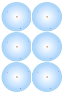
1 mol lithium ≈ $6{\cdot}10^{23}$ Li atoms
1 mol hydrogen ≈ $6{\cdot}10^{23}$ H_2 molecules = $12{\cdot}10^{23}$ H atoms
1 mol helium ≈ $6{\cdot}10^{23}$ He atoms

Representation: 1 particles ⇒ 10^{23} particles

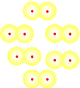


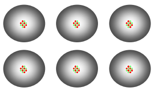
1 mol water
$6{\cdot}10^{23}$ molecules
(2+16 = 18 g)

1 mol lithium
$6{\cdot}10^{23}$ atoms
(7 g)

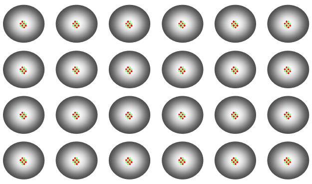


1 mol hydrogen
$6{\cdot}10^{23}$ molecules
(2 g)





1 mol carbon
$6{\cdot}10^{23}$ atoms
(12 g)



4 mol carbon
$4{\cdot}6{\cdot}10^{23}$ atoms
(48 g)

Calculating with the Amount of Substance

The mass *m* [g] and the amount of substance *n* [mol)] can be converted by the molar mass *M* [g/mol]:

$$\begin{tikzcd} & M = \frac{m}{n} \arrow[dl, leftrightarrow] \arrow[dr, leftrightarrow] & \\ m = M \cdot n \arrow[rr, leftrightarrow] & & n = \frac{m}{M} \end{tikzcd}$$

Examples:

What is the mass of 0,2 mol glucose?

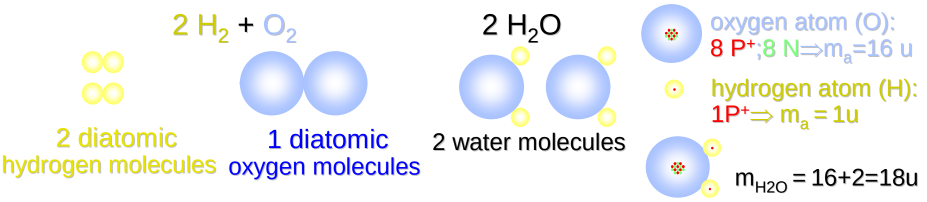
$$m = 180g/mol \cdot 0{,}2mol = 36g$$

What is 5,85 g Sodium chloride (NaCl) in Mol?

$m_A(Na)$ = 23 u; $m_A(Cl)$ = 35,5 u ⇒ M_{NaCl}= 58,5 g/mol

$$n = \frac{5{,}85g}{58{,}5g/mol} = 0{,}1mol$$

Illustration of Stoichiometry and Molar Mass



A water molecule (H_2O) consists of 2 hydrogen and 1 oxygen atoms.
The reactants must contain twice as much H atoms as O atoms.
Both elements are diatomic molecules.

Molar Masses: $M(H_2)$=2 g/mol; $M(O_2)$=32 g/mol; $M(H_2O)$=18 g/mol

Hydrogen +	Oxygen =	Water
2 molecules (2·2u = 4u)	1 molecule (2·16u=32u)	2 molecule (2·18u=36 u)
2000 molecules	1000 molecules	2000 molecules
2 mol (2·6 ·10^{23} molecules)	1 mol (6·10^{23} molecules)	2 mol (2·6·10^{23} molecules)
4 g +	32 g =	36 g

Conservation of mass!

Molar Volume of Gases

1 Mole of any gas contains always 6·10^{23} particles,
either atoms (noble gases, e. g. He),
or diatomic molecules (other gaseous elements: H_2, N_2, O_2, F_2, Cl_2)
or compound molecules (e. g. CO_2).

1 Mole of ideal gas has a volume of V = 22,4 L under STP.

Molar volume of gases: V_m = 22,4 L/mol :

Example: A volume of 1,12 L of gas contains which amount of substance *n* [mol]?

$$n = \frac{V}{V_m} = \frac{1{,}12L}{22{,}4\,L/mol} = 0{,}05mol$$

Concentration - Molarity

Many chemical reactions in solvent (e. g. water)
How many reactant particles are in the solution?

The molar concentration $\boldsymbol{c}$ defined as amount of a constituent $\boldsymbol{n}$ divided by the volume of mixture (or solvent*) $\boldsymbol{V}$

$$c = \frac{n}{V}$$

*Dissolving a substance in a solvent does not change the volume significantly. The density is increased.

Examples:

2 Mole of a substance are dissolved in 500 mL solvent. c = ?

$$c = \frac{2mol}{0{,}5L} = 4mol/L$$

Which amount of substance has to be dissolved in 200 ml, yielding a solution ?

$$n = c \cdot V = 0{,}5mol/L \cdot 0{,}2L = 0{,}1mol$$

2 Mole have to be dissolved in how much solvent, so that c = 0,1 mol/L?

$$V = \frac{n}{c} = \frac{2mol}{0{,}1mol/L} = 20L$$

1,8 g glucose in 100 ml water; c = ?.

$$n = \frac{m}{M} = \frac{1{,}8g}{180g/mol} = 0{,}01mol = 10^{-2}mol \qquad c = \frac{0{,}01mol}{0{,}1L} = 0{,}1mol/L$$

Isotopes

Isotopes are variants of atoms of a particular chemical element, differing in the numbers of neutrons and in the atomic mass.

They contain the same number of protons,
but a different number of neutrons.

Examples:

Hydrogen: $^{1}_{1}H$ Deuterium: $^{2}_{1}H$

Carbon: $^{12}_{6}C$ ~99% nat. abundance; $^{13}_{6}C$ ~1%

Traces of $^{14}_{6}C$; instable ⇒ radioactive
(Radiocarbon dating)

Uranium: $^{235}_{92}U$ fissile; $^{238}_{92}U$ non fissile, both radioactive

Isotopes have identical chemical properties (bonding),
but different physical properties (mass)

Non-whole Number Masses

The atomic masses of many elements in the PSE are,
non-whole numbers, since they consist of mixtures of isotope.

Example: Chlorine, average atomic mass = 35,45 u

consists of:

- ^{35}Cl: 75.7%
- ^{37}Cl: 24.2%

Calculation:

$$0{,}757 \cdot 35 + 0{,}24 \cdot 37 = 35{,}45$$

Elements that form only one stable type of atom (isotop)
are named ***pure elements***.

Example: ^{19}Fluorine

Ions

Atoms contain as many electrons in the shell as protons
in the nucleus and are consequently neutral.

Ions are atoms or molecules in which the number of electrons
is not equal to the total number of protons,
giving it a net positive or negative electrical charge.

Ions have completely different properties than the resp. atoms !

Examples: $Na \rightarrow Na^+ + e^-$ ***Positive*** ions = ***cations***,

$Cl + e^- \rightarrow Cl^-$ ***Negative*** ions = ***anions***.

Cations derived from metal name (sodium (cat)ion, silver (cat)ion)
or have the suffix –***ium*** (NH_4^+ = ammonium ion)

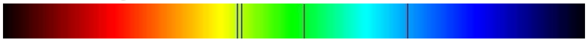
Anions from non-metal atoms have the suffix –***ide*** (chloride)
in compounds with oxygen –***ate*** (SO_4^{2-}=sulfate) or –***ite*** (SO_3^{2-}=sulfite)

Ions can carry multiple charges: Examples: Al^{3+}, O^{2-}

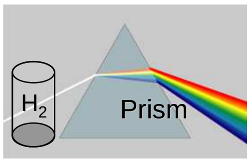
Review of Rutherford Model

Rutherford´s model makes no statement about the electron-structure of the atom or the energy of the electrons in the shell; it does not explain the differences in chemical behavior of the elements .

Experiment: Hydrogen absorbs specific colors = wave length from the spectrum of visible light

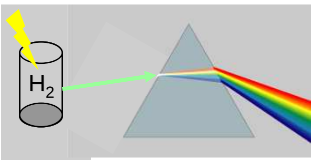


Absorption spectrum of hydrogen



Vice versa, thermally activated hydrogen emits light of exactly the same wave lengths.

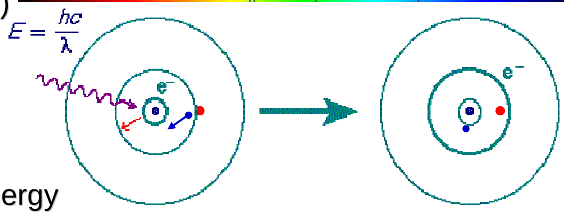
Emissions spectrum of hydrogen



Why specific wave length = energies?

Discrete Energy Levels of Electrons

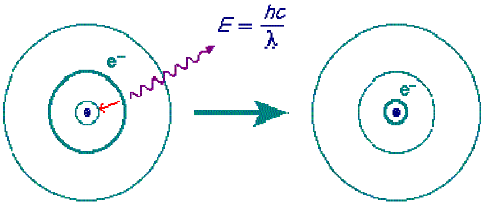
Electrons can occupy different well-defined (=discrete) energy levels in the shell. Transition between level by absorption or release of energy
(net energy conservation)



Excitation of atom by light

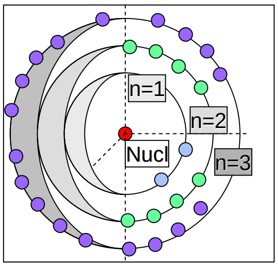
Excitation: By additional energy (heat, photon, electricity) the electron can be moved to higher level (outer orbit).
If photon energy too high
⇒ ionization

Deactivation of excited electrons under emission of electromagnetic wave and return to lower level
(inner orbit).



Deactivation by emission of light

Bohr Model



Electrons travel around nucleus in circular orbits (shells) associated with definite energy levels with the principle quantum number n.
The orbit radius r and the electron energy increases as n^2.

The shells are filled with electrons from inside (lowest energy level) to outside.

Shell	n	elec-trons
K	1	2
L	2	8
M	3	18
N	4	32

Each shell can carry a certain number of electrons:

$$\boxed{2 \cdot n^2}$$

In the heaviest atoms
7 shells are occupied.


Niels Bohr, Dan. phys
Atomic model 1913
Nobel prize 1922

Only the electrons of the *outermost (valence-) shell* can participate in formation of chemical bonds.

Electron Configuration

Element	Z	n=1 max. 2	n=2 max. 8	n=3 max 8+10	n=4
H	1	1			
He	2	2			
Li	3	2	1		
Be	4	2	2		
F	9	2	7		
Ne	10	2	8		
Na	11	2	8	1	
Mg	12	2	8	2	
Cl	17	2	8	7	
Ar	18	2	8	8	

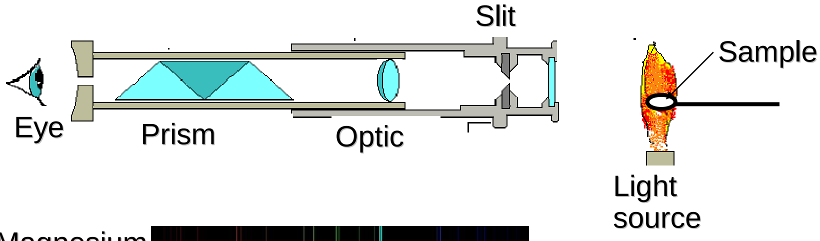
Complete (closed) shells

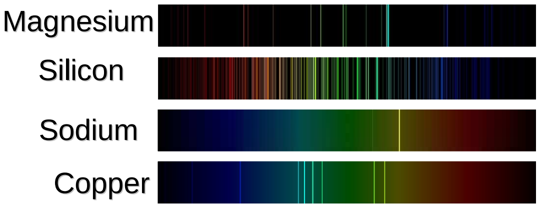
Valence electrons

The number of valence electrons determines chemical properties!

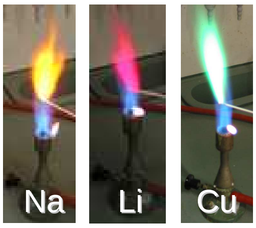
Atomic Emission Spectrometry
Flame Photometry

Each element has its unique ***electron configuration*** and hence characteristic electron transitions and corresponding lines in the emission spectrum ⇒ atomic emission spectrometry.

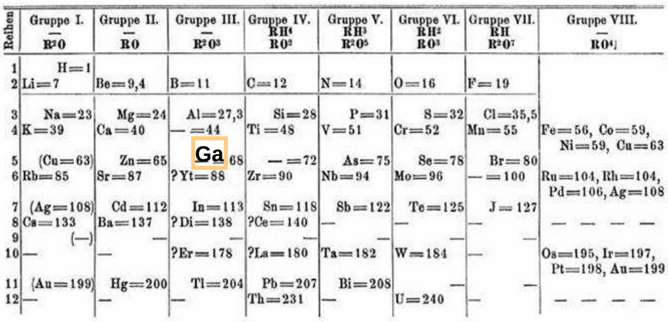




Even without spectrometer some elements can be distinguished by the color of the flame:



Periodic Table (System) of Elements
Prediction of Elements by Mendeleev



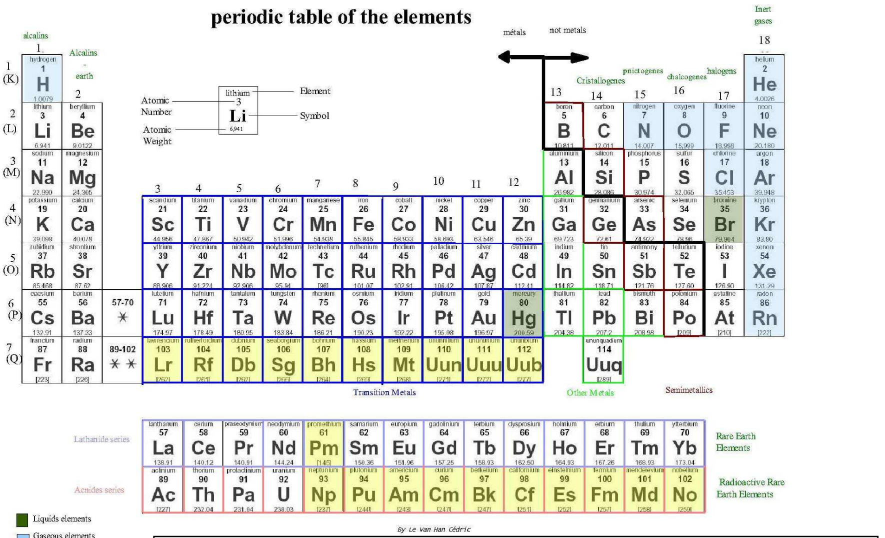
Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	— =44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
5	(Cu=63)	Zn=65	Ga 68	— =72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	— =100	Ru=104, Rh=104, Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Dimitri Mendeleev
Periodic table
(1869)

<u>Properties of Gallium (Ga)</u>

	Prediction	Reality
Atomic mass	~ 68	69,72
Density	~ 5,9 g/cm^3	5,91 g/cm^3
Melting Temp.	~ 30℃	29,8℃
Oxide	X_2O_3	Ga_2O_3
Chloride	XCl_3	$GaCl_3$

Periodic Table of Elements

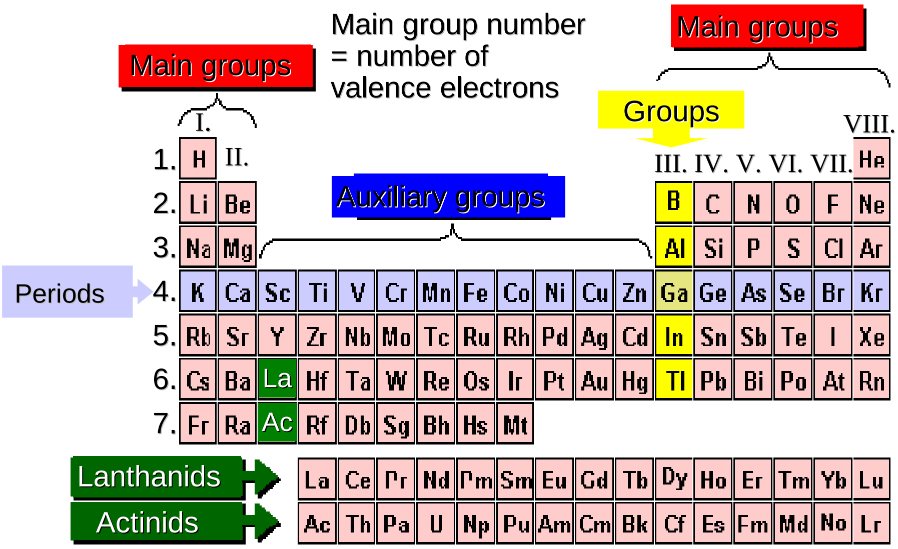


	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 (K)	1 H																		2 He
2 (L)	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3 (M)	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4 (N)	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5 (O)	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
6 (P)	55 Cs	56 Ba	57-70 *	71 Lu	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
7 (Q)	87 Fr	88 Ra	89-102 * *	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub		114 Uuq				

Lathanide series	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
Actnides series	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Elements listed with increasing value of atomic number = no. Protons in nucleus = no. electrons in shell.

Structure of Periodic Table

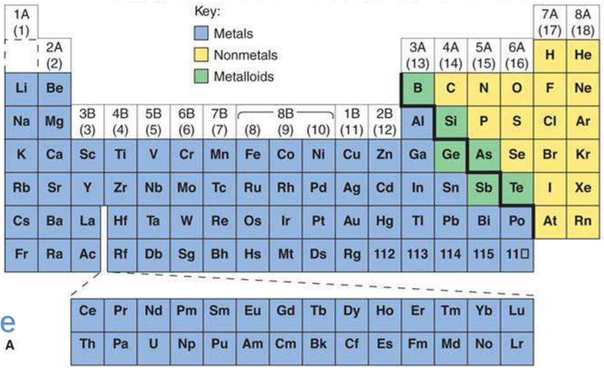


Main group number = number of valence electrons

	I.	II.											III.	IV.	V.	VI.	VII.	VIII.
1.	H																	He
2.	Li	Be											B	C	N	O	F	Ne
3.	Na	Mg											Al	Si	P	S	Cl	Ar
4.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5.	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6.	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7.	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt									

Lanthanids	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinids	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Metals, Metaloids (Semimetals), Non-metals



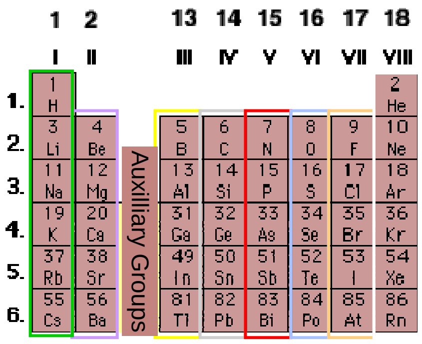
- isolators (exept carbon as graphite)
- gaseous or low melting
- brittle solids

- conductive
- solid (except mercury) some high melting
- malleable, ductile

Metallic character of elements in the periodic table decreases from bottom left to top right.

> 80% of the elements are metals.

Main Group Elements



I. <u>Alkali metals</u>: silver, low melting, soft <u>Highly reactive</u>, natural abundance **only in compounds**, not elemental.

II. <u>Alkali earth metals</u>: like alkali, but less reactive (stable in air).

III. <u>Boron group</u>: B hard metalloid, Al→Tl soft metals. Al-compounds highly abundant in Earth´s crust.

IV. <u>Carbon group</u>: C nonmetal, Si,Ge metaloids; Sn, Pb met.; different properties. Si high abundance (quartz); C→natural compounds; Pb high density.

V. <u>Nitrogen group</u>: N=non-metall (gaseous) P/As met. and nonmet. allotropes, Sb/Bi=met.; N main ingredient air 78%

VI. <u>Chalcogens</u>: O gaseous, nonmetal,vital in water; 21% of air). S yellow solid Se, Te, Po metalloid/metal allotropes

VII. <u>Halogens</u>: all nonmetals F/Cl gas, Br liquid, I solid **reactive; form salts with I and II**

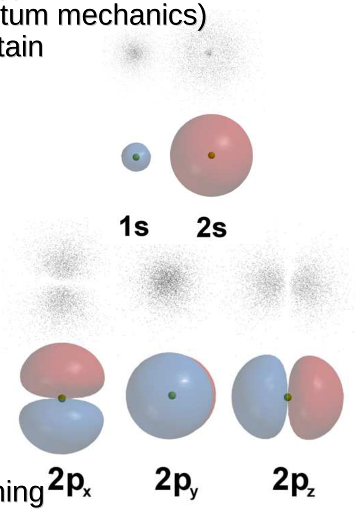
VIII. <u>noble (inert) gases</u>: **extremely low reactivity** → elemental state: as traces in air

Orbitals

Flaw of Bohr´s model: A circulating charged particle emits radiation
→ energy loss; and: experiments indicate electron has wave character.
⇒ **Orbital model:** Atomic orbitals are (energy) states
or wave forms of electrons in the atom (quantum mechanics)
The probability of finding an electron in a certain
volume of space is the **electron density.**
s-, p-, d-, and f-orbitals exist:

s-orbitals are spherical.
The K-shell (n=1; 2 e^-) has only 1s-orb.
In the 2. shell (L-shell, max. 8 e^-)
at first the 2s-orbital (max. $2e^-$), afterwards
the p-orbitals are occupied.
p-orbitals dumbbell shaped.
There are three: p_x, p_y, p_z
having the same energy state.
Each contains max. 2 e^-

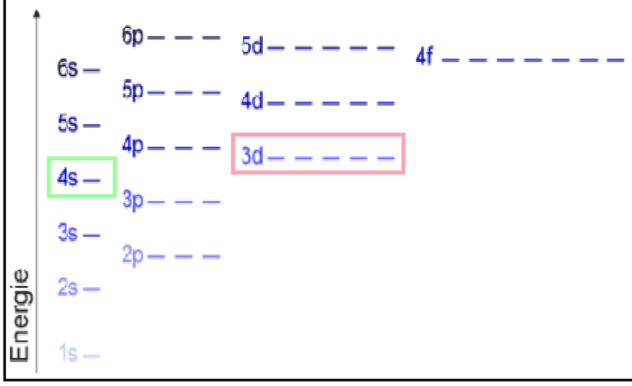
Every next shell ⇒ new type of orbital
(more complex shape). s, p, d hist., no meaning

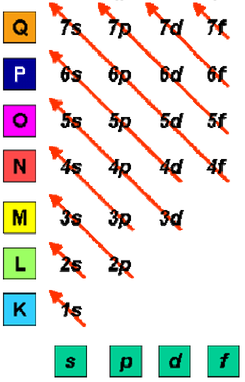


Energy Levels of Orbitals

Main energy levels ("shells"): 1, 2, 3, 4, 5, 6
Within each shell the energy level s- < p- < d-orbital.
Electrons fill low energy orbitals before they fill higher energy ones.
3. and 4. main energy level overlap ⇒
4s-orbitals are filled before the 3d-orbitals

(see PSE: After K, Ca (s-block), introduction of transition metals with valence electrons in d-orbitals. Afterwards Ga,Ge,As etc. (p-block)





Quantum Numbers

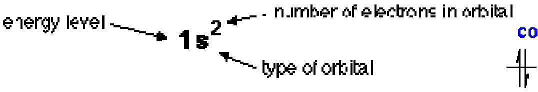
Quantum numbers describe the energy of electrons in atoms.

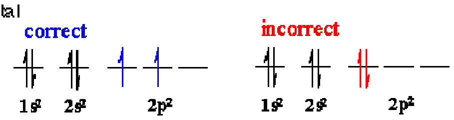
Name	Symbol	Orbital meaning	Range of Values	Value Example
Principal (prim.) q.n.	n	shell (main energy level)	$n \geq 1$	$n = 1,2,3,...$
Azimuthal q.n. (angular momentum)	l	subshell: $s \Rightarrow 0$ (orbital) $p \Rightarrow 1$ $d \Rightarrow 2$	$0 \leq l \geq n\text{-}1$	for $n = 3$: $l = 0,1,2$ (s,p,d)
Magnetic q.n. (Projection of angular momentum)	m_l	orientation of subshell shape	$-l \leq m_l \geq +l$	for $l = 1$ (p-Orb.) $m_l = -1,0,+1$ p_x,p_y,p_z
Spin q.n.	m_s	Spin of electron	½ : clockwise -½: counter-clockwise	

Fitting Electrons into Orbitals Pauli Principle/Hund´s rule

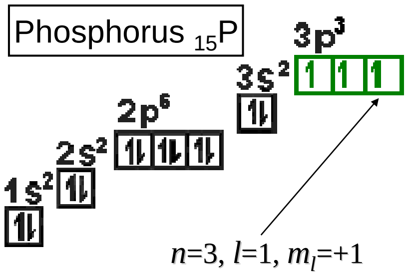
Pauli principle: Two electrons my not occupy same quantum state⇒ Each orbital occupied by max. two electrons with different spin ↑↓.

Hund´s rule: When several orbitals of equal energy are available, electrons enter singly with parallel spins (minimizes repulsion).

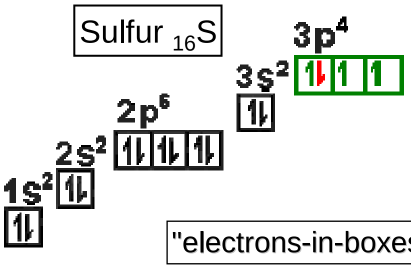




Examples:



n=3, l=1, m_l=+1



"electrons-in-boxes"

"Full" Outer Valence Shell Noble Gas Configuration

The number of valence electrons (VE) in the outer shell determines the chemical behavior.

"Full", closed-shell configuration have a favorable low energy.

Elements with a closed-shell (no valence electrons) (18. group or VIII. main group: He, Ne, Ar, etc.) show very little tendency to participate in chemical reactions
Since they are all gases they are called ***noble*** *(or inert)* ***gases***.

Electron configurations with a closed-shell are called noble gas configuration.

Atoms of other elements can reach lower energy states by undergoing chemical reactions. By loss or gain of electrons they can reach a ***noble gas electron configuration***.

Noble Gas Configuration/Octet Rule Examples

Octet rule (of thumb): Atoms tend to combine in a way that they each have eight electrons in their valence shells, giving them the same electronic configuration as a noble gas (applicable to the main-group elements, except helium).

Examples:

Noble gas: ${}_{10}\mathrm{Ne}$ $1s^2\,|\,2s^2\,2p^6$

$${}_{11}\mathrm{Na}\ (1s^2\,|\,2s^2\,2p^6\,3s^1) \xrightarrow{-e^-} \mathrm{Na}^+\ (1s^2\,|\,2s^2\,2p^6)$$

$${}_{9}\mathrm{F}\ (1s^2\,|\,2s^2\,2p^5) \xrightarrow{+e^-} \mathrm{F}^-\ (1s^2\,|\,2s^2\,2p^6)$$

Atoms that lose electrons have less negative charges in shell than positive protons in the core and become positive cations.

Atoms that gain electrons become negative anions.

More Examples for Noble Gas Configuration

Potassium ($_{19}$K, alkali) looses 1 e^-, becomes K^+ cation, with the same electron configuration like Argon $_{18}$Ar. Its chemical and physical properties are of cause completely different (different number of protons).

The same electron configuration achieves chlorine ($_{17}$Cl, halogen) by gaining 1e^- becoming Cl^- (chloride ion).

In a similar manner calcium ($_{20}$Ca, alkali earth metal) can lose two e^- $\Rightarrow Ca^{2+}$, or $_{16}S + 2\,e^- \rightarrow S^{2-}$
both ions have the same electron configuration as $_{18}$Ar

By loss or gain of electrons particles reach the favorable, low energy closed-shell (noble gas configuration).

Chemical Bonds + Molecules Types of Bonds

When atoms of different elements form chemical compounds, their chemical and physical properties change significantly.

Example:

+

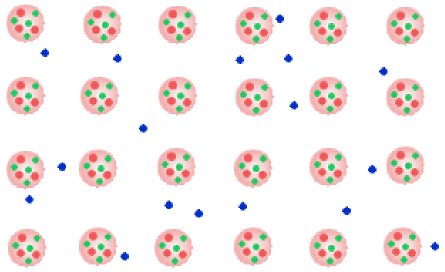
→

Three types of chemical bond

nonmetal-nonmetal	metal with non-metal (often)	metal with metal	
Covalent bond	Ionic bond	metallic bond	coordinate bond
↓	↓	↓	
molecules	salts	metals (alloys)	metal complexes
e. g. H_2O	e.g. Na^+Cl^-	e. g. bronze	

Metallic Bonding

Metallic bonding: Electrostatic attractive force between positively charged cations (nucleus + inner e^-), which form a 3D lattice and negative, delocalized, shared valence electrons ("electron sea").



The free mobility of the valence electrons causes electrical conductivity of metals.

Metal bonding exists between atoms of a pure metal, as well as in blends of two or more metals (alloys).

Common alloys: bronze = copper/tin; brass= copper/zinc
Rose gold=gold/copper; white gold=Au-Ag/Ni/Pd
Amalgam: mercury/silver

Ionic Bond
Ionization

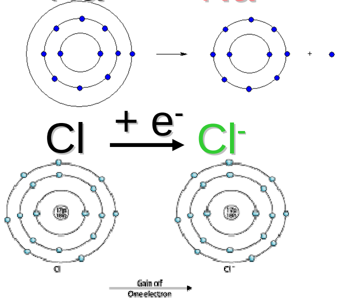
When atoms lose or gain electrons, ions are formed:
Ions with positive charge are called **cations**.
They have lost electrons.

In return, **anions** have gained electrons to fill their valence shell.
They are negatively charged.

The atomic number (number of protons in nucleus) does not change.
The mass does not change significantly.

$$\mathrm{Na} \xrightarrow{-\,e^-} \mathrm{Na}^+$$

$$\mathrm{Cl} \xrightarrow{+\,e^-} \mathrm{Cl}^-$$

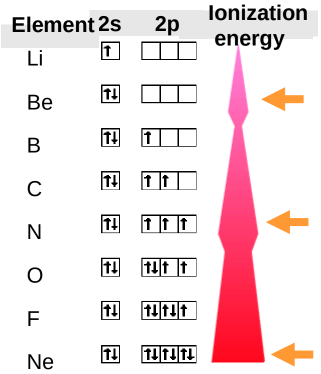


Whether an atom tends to lose or gain one or more electrons depends on the related change of its energy level.
The system as a whole strives to achieve the **lowest energy state**.

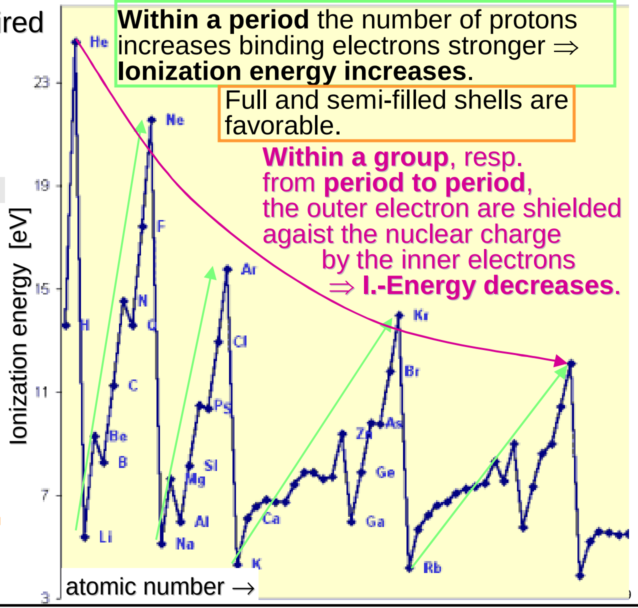
Metals tend to lose electrons –
nonmetals tend to gain electrons.

Ionization Energy

Ionization I energy required to remove an electron from an atom.
⇒ cation
(Unit: eV = 1,6·10^{-19} J)



Element	2s	2p	Ionization energy
Li	↑	☐☐☐	
Be	↑↓	☐☐☐	
B	↑↓	↑ ☐☐	
C	↑↓	↑ ↑ ☐	
N	↑↓	↑ ↑ ↑	
O	↑↓	↑↓ ↑ ↑	
F	↑↓	↑↓ ↑↓ ↑	
Ne	↑↓	↑↓ ↑↓ ↑↓	



Within a period the number of protons increases binding electrons stronger ⇒ **Ionization energy increases**.

Full and semi-filled shells are favorable.

Within a group, resp. from **period to period**, the outer electron are shielded agaist the nuclear charge by the inner electrons ⇒ **I.-Energy decreases.**

Electron Affinity

The **electron affinity** EA is the counter part of the ***ionization energy***. Amount of energy *released* when an electron is added to an atom
⇒ negative anion.

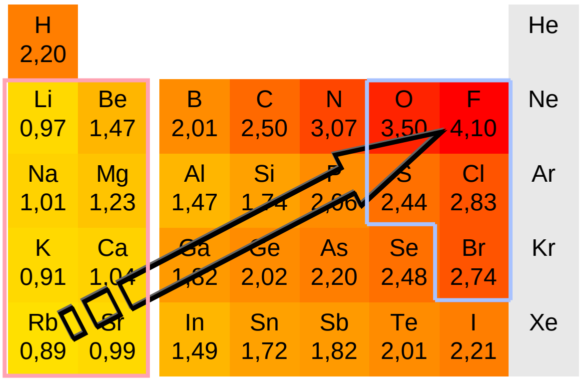
Positive values:
System would go to higher energy state ⇒ gain of electrons not possible.
Negative EA-values:
Energy is released.
Halogens and chalcogens have high electron affinities
⇒Large amounts of energy is released, if they gain electrons.

Electron affinities (eV)

H -0.75							He >0
Li -0.62	Be >0	B -0.28	C -1.26	N +0.07	O -1.46	F -3.40	Ne >0
Na -0.55	Mg >0	Al -0.44	Si -1.28	P -0.75	S -2.08	Cl -3,62	Ar >0
K -0.5	Ca >0	Ga -0.3	Ge -1.2	As -0.81	Se -2.02	Br -3.36	Kr >0
Rb -0.49	Sr >0	In -0.3	Sn -1.2	Sb -1.07	Te -1.97	I -3.06	Xe >0
Cs -0.47	Ba >0	Tl -0.2	Pb -0.36	Bi -0.95	Po	At	Rn
Fr	Ra						

Electronegativity (EN)

Electronegativity (EN) describes the tendency of an atom (or a functional group) to attract electrons (or electron density) towards itself.



H 2,20							He
Li 0,97	Be 1,47	B 2,01	C 2,50	N 3,07	O 3,50	F 4,10	Ne
Na 1,01	Mg 1,23	Al 1,47	Si 1,74	P 2,06	S 2,44	Cl 2,83	Ar
K 0,91	Ca 1,04	Ga 1,82	Ge 2,02	As 2,20	Se 2,48	Br 2,74	Kr
Rb 0,89	Sr 0,99	In 1,49	Sn 1,72	Sb 1,82	Te 2,01	I 2,21	Xe

EN increases from bottom left to top right in the PSE

Alkali (I. MG) and alkali earth metals (II. HG) electropositive. ⇒ Ionic bonds with halogens (VII. MG) and chalcogens (VI. HG)

For organic chem.: Hal/O >> C > H

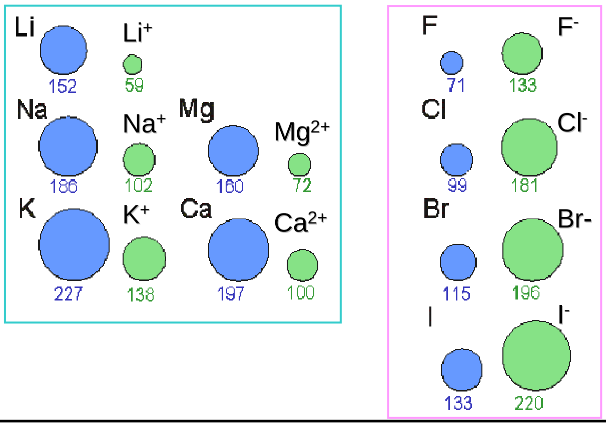
Larger difference in EN ⇒ more polar bond; ΔEN>1,5 ⇒ ionic

Compounds of alkali-/alkali earth metals and chalcogens resp. halogens are ionic as a rule of thumb.

Atomic and Ionic Radius

Gain or loss of electrons alters the radius of the particle.
The radii of atoms and their respective ions are significantly different.
Loss of electrons (⇒ cation) decreases the radius,
since the residual electrons are attracted more by the nuclear charge.
Gain of electrons (⇒ anion) increases the radius, since the electron shell becomes wider by the additional negative charge.

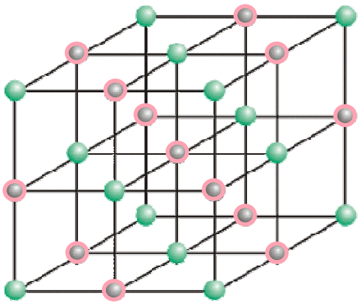
Examples:

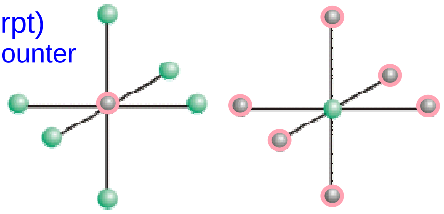


Salts, Ionic Lattice

Salts are solids, that consist of ions (ionic bond).
Cations (+) and anions (-) are attracted by ***electrostatic forces***. The ions are positioned in a three-dimensional ***crystal lattice*** with regular long-range order.
Such ionic crystals have high melting temperatures, are hard + brittle.

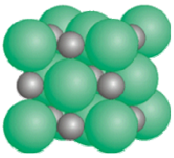
Example: NaCl crystal (excerpt)
Each ion is surrounded by six counter ions in octahedral geometry





● Na^+
● Cl^-

With consi-deration of the ionic radius.



Chemical Formulas of Salts

The ionic crystal lattice is a continuous structure with no overall charge (***electrical neutral).*** Positive charges of cations are compensated by negative charges of anions ⇒ defined molar ratio (stoichiometry) of ***cations and anions***.
Since cations and anions can carry different amounts of charge, their ratio can differ from 1:1.

General composition of a salt: $\{x \cdot A^{n+}\ y \cdot B^{m-}\} = A_xB_y$ x resp. y = 1 omitted

Ionic notation (displays charges) Empirical formula (only molar ratio)

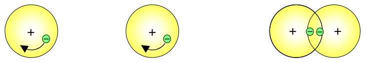
Examples:

Combination of ions in compound so that charges are compensated

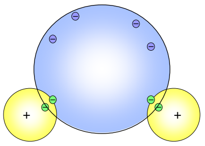
Elements in compound		Ions with closed-shell		Formula		Name of salt
Na	Br	Na^+	Br^-	$NaBr$	$\{Na^+Br^-\}$	sodium bromide
K	S	K^+	S^{2-}	K_2S	$\{2K^+S^{2-}\}$	potassium sulfide
Ca	O	Ca^{2+}	O^{2-}	CaO	$\{Ca^{2+}O^{2-}\}$	Calcium oxide
Ba	Cl	Ba^{2+}	Cl^-	$BaCl_2$	$\{Ba^{2+}2Cl^-\}$	Barium chloride
Al	F	Al^{3+}	F^-	AlF_3	$\{Al^{3+}3F^-\}$	Aluminum fluoride
Al	O	Al^{3+}	O^{2-}	Al_2O_3	$\{2Al^{3+}3O^{2-}\}$	Aluminum oxide

Covalent Bond

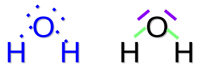
Atoms with low EN differences can form **shared pair of electrons**
The electron shells (or orbitals) overlap ⇒ **covalent bond**.
⇒ molecules



H-atoms H$_2$-molecule



Examples:

Compound	Emp. formula	Structural formula
Hydrogen	H_2	H:H H-H
Hydrogen fluoride	HF	
Water	H_2O	

* H forms exclusively covalent bonds, because no free H^+ (proton=elemental part.)

Valence electrons not involved in covalent bonds form **free (or lone) electron pairs.**

Octet rule (of thumb): Atoms tend to combine in a why that they each have 8 electrons (4 electron pairs) in their valence shell

---

Bond Character

The presented types of bonds are only models.
Real bonds can be intermediates; bond character varies continuously throughout the PSE.

Examples:

Compounds of chlorine with elements of the 3. period:

NaCl $MgCl_2$ $AlCl_3$ $SiCl_2$ PCl_3 SCl_2 Cl_2

Ionic bond Covalent bond

Compounds of sodium with elements of the 3. period:

Na NaMg NaAl NaSi Na_3P Na_2S NaCl

Metallic bond Ionic bond

Elements of the 3. period

Na Mg Al Si P_4 S_8 Cl_2

Metallic bond Covalent bond

Chemical Compounds
Molecules, Molecular Mass

A molecule is an electrically neutral group of at least two atom
(of same or different element) held together by covalent chemical bonds

All gaseous elements* form diatomic molecules:
H_2, N_2, O_2, F_2, Cl_2

*besides noble gases

The nonmetals bromine (liquid) and iodine (solid) too: Br_2, I_2

The molar mass of a molecule is the sum of the molar masses of the constituting atoms.

Examples: Formula	Molar mass of atom	Molar mass [g/mol]
HCl	H=1,00 Cl=35,45	1,00 + 35,45 = 36,45
CH_4	H=1,00 C=12,01	12,01 + (4·1,00)=16,01
H_2SO_4	S=32,07 O=16,00	(2·1)+32,07+(4·16)=98,07

Stoichiometric Valency

The valency is a measure of the number of bonds formed by a given element. It depends on the number of valence electrons.

Rules:
- H has always valence number 1
- Alkali metals (I. MG.) have always valence number 1
- Alkali earth metals (II. MG) always 2
- Elements of III. MG have valency 3
- Halogens (VII. MG: F, Cl, Br, I) are always single valent
- O very often valency 2
- Other elements different valency (MG. elements max. 4)
- Products of lower case indices and valency in binary compounds constant (last example)

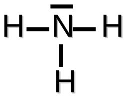
Examples: H_2O: 2-valent oxygen binds two single valent H
NaCl: Both single valent ⇒ combine 1:1
$MgCl_2$: 2-valent Mg binds 2 single valent Cl
Al_2O_3: 2·Al (3-valent): 2·3 = 6; 3·O (2-valent): 3·2 = 6

Chemical/Structural Formulas of Molecules
Single/Double/Triple Bonds

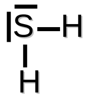
Chemical (empirical) formula: Simplest whole number ratio of atoms of each element present in a compound.

Structural formula: Graphical representation of molecular structure, showing ***how*** the atoms are ***arranged.***
= Valence structure = LEWIS formula
All valence electrons (bonding and lone electron pairs) represented.

More examples: Ammonia NH_3

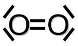


Hydrogen sulfide H_2S

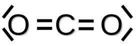


Some compounds (in particular of C, N, and O) contain double or triple bonds:

Examples: Oxygen



Carbon dioxide



Nitrogen

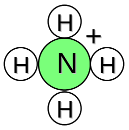
Check valency and octet rule!

Polyatomic Compound Ions

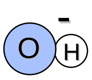
Ions can also be formed from groups of joined atoms: Compound ions

Most common compound ions:

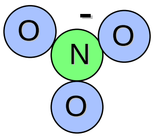
Ammonium ion NH_4^+



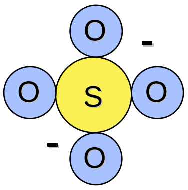
Hydroxide ion OH^-



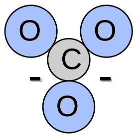
Nitrate ion NO_3^-



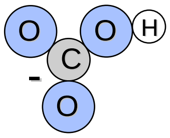
Sulfate ion SO_4^{2-}



Carbonate ion CO_3^{2-}

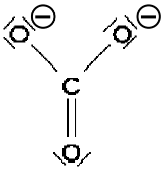


Hydrogen carbonate ion HCO_3^{2-}



Chemical Models
Mesomeric Resonance

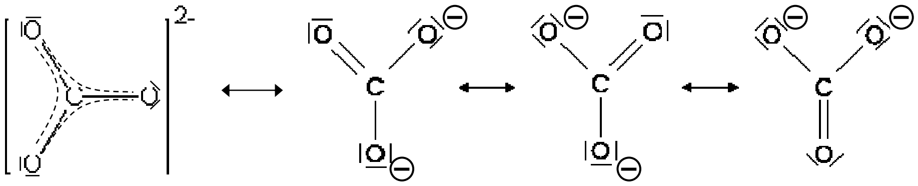
Rene Margritte:
"This is no apple"



"This is no carbonate ion !"

It is a (crude!) model
of a carbonate ion.
Experiments indicate:
All O-atoms same charge;
all bonds identical;
all bond angles identical.

Christopher Ingold (1933): Mesomerism = Representation of delocalized electrons by different contributing structures.



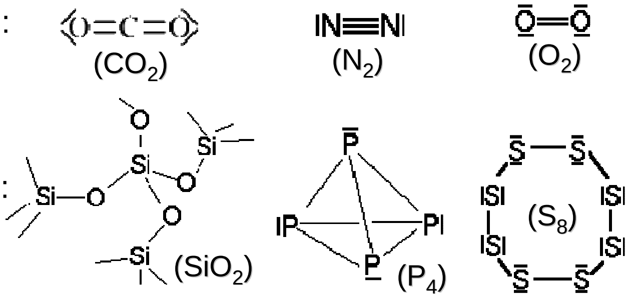
Double Bond Rule
(empirical)

Elements of the second period (C, N, O) often form double bonds. The analogous elements of the 3. period (and higher), however, form in analogous compounds form preferably single bonds.

Main group: → IV. V. VI.

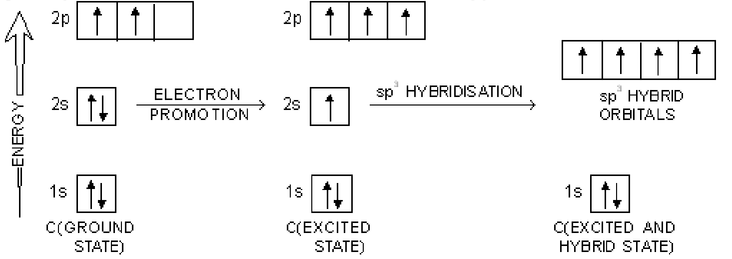
2. Period:

3. Period:



Bond Theory
Orbital Hybridization (sp^3)

Carbon essential element in organic compounds; forms covalent bonds.
C has 4 electrons in valence shell: configuration $2s^2\ 2p^2$ (ground state)
1 lone electron pair (s^2) and 2 p-electron could form only 2 bonds.
Prediction: CH_2 But: Carbon is 4-valent! Example.: CH_4 ?!
Explanation: The valence electrons are rearranged in a way, that 4 electrons can form bonds.
The s-orbital and the three p-orbitals are mixed to form ***four sp^3-hybrid orbitals*** of identical energy.



Hybridization is not a physical fact -,
it's only an model to explain experimental observations!
(e. g. molecule geometry) !

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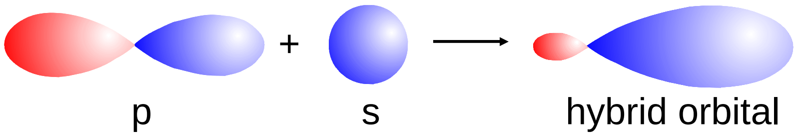
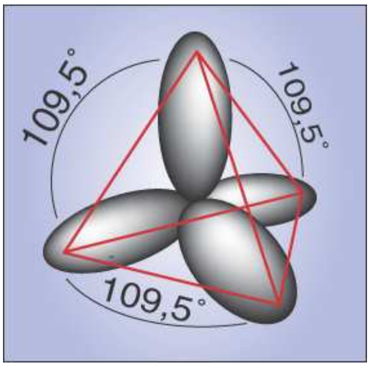
sp^3-Hybrid Orbitals

Geometry of hybrid orbitals

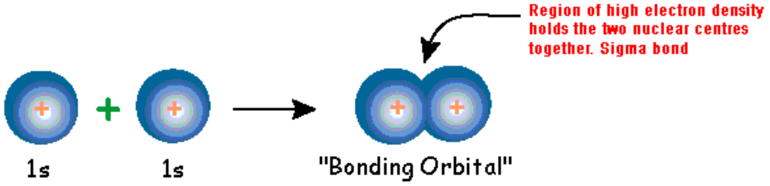


The 4 *sp^3* hybrid orbitals arranged in space with a maximum separation: **tetrahedral**



Single Bonds

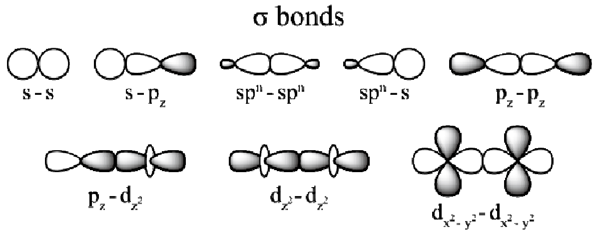
Two hydrogen atoms form a single bond (σ ***-bond)*** by head-on overlapping between the atom orbitals.



Region of high electron density holds the two nuclear centres together. Sigma bond

Highest electron density between the two nuclei.
σ-bond is symmetrical with respect to rotation about bond axis.

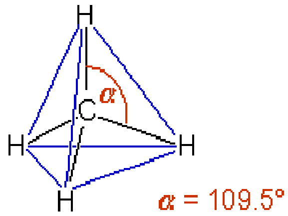
Other orbitals can also form σ-bonds:



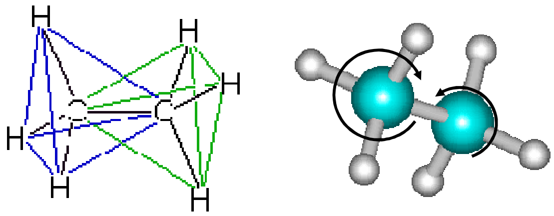
Single Bonds in Hydrocarbons

C-H-bonds and C-C single bonds are σ-bonds.
Four σ-bonds ⇒ complies with octet rule.

Example:
Methane
4 C-H-
σ-bonds



Example:
Ethane
3 C-H-
1 C-C-
σ-bonds

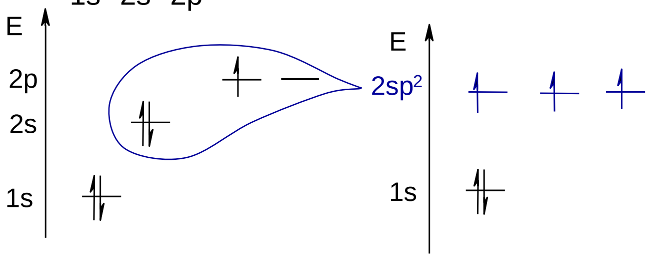


Free rotation about σ-bonds

sp^2-Hybridisation
Example: Boron

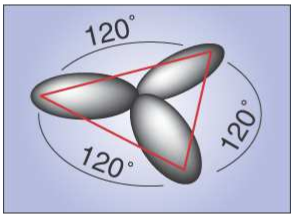
Boron (ground state): $1s^2\ 2s^2\ 2p^1$

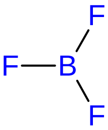
hybridization:



One s- and two p-orbitals mix to form tree sp^2 hybrids of equivalent energy each occupied by one electron

Trigonal-planar geometry of three sp^2-hybrid orbitals in space.





Boron trifluoride (BF_3) does **not** comply with octet rule
⇒ electron gap
⇒ Lewis acid

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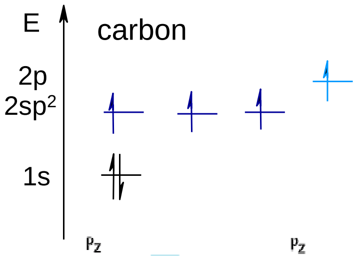
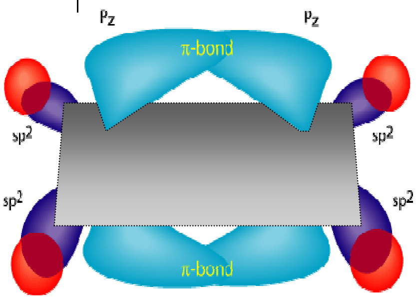
sp^2-Hybridisation of Carbon



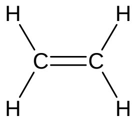
The 2s-orbital and the two 2p-orbitals mix to form three sp^2-hybrid orbitals.
The third p-orbital unaffected.
Each occupied with single electron.



sp^2-hybrid orbitals of carbon and bonds formed in ethene.

In an ethene molecule three sp^2-hybrid electrons form three σ-bonds: Two with the H-atoms and one with the other C-atom (trigonal-planar).

The fourth electrons occupy the remaining, unhybridized p_z-orbitals, sidewise overlapping above ***and*** beneath the plane to form a ***π-bond***.

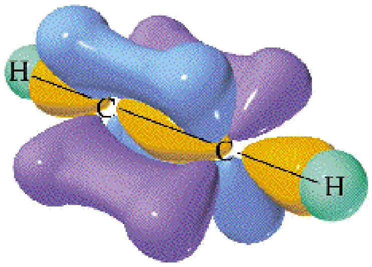


C-C-σ-bond and ***π-bond*** together form double bond.

sp-Hybridization

Which elements can mix one s- and one p- orbital to two sp hybrids to form two σ-bonds and how are they arranged in space?

Beryllium (II. main group) can form two sp-hybrid orbitals, which can form two σ-bonds (linear, 180°) e. g.: H-Be-H



sp-hybrid orbitals of carbon and bonds formed in ethyne.

The two sp-hybrids of each C-atom form two σ-bonds (C-C and C-H). The two remaining p-orbitals overlap crossbred sidewise to form two C-C π-bonds.

One C-C σ-bond and two π-bonds together form a triple bond:

$$H-C\equiv C-H$$

Polar Covalent Bonds
Dipolar Molecules

A polar bond is a covalent bond between two atoms with different electronegativities ΔEN>0.
The electron density of the bonding electron pair is higher in the vicinity of the atom with the higher electronegativity.
Partial charges and a permanent dipole are formed.

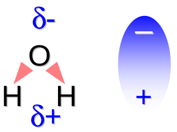
$$\overset{\delta+}{H}\rightarrow\overset{\delta-}{Cl} \qquad H\blacktriangleleft Cl$$

EN: 2,2 2,8

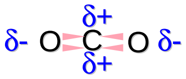
$\longmapsto$ Dipolar momentum

EN (O): 3,5

EN (H): 2,2



Water molecule angled ⇒
partial charges asymmetrical
⇒ dipole molecule
⇒strong intermolecular forces
⇒ liquid (high boiling temp.)



$$\delta-\ O=\overset{\delta+}{\underset{\delta+}{C}}=O\ \delta-$$

Carbon dioxide: linear
partial charges symmetrical
⇒ **no** dipolar molecule
⇒weak intermolecular forces
⇒ gas (low boiling temp.)

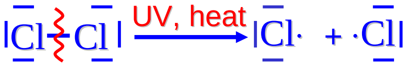
Cleavage of Covalent Bonds

Before new bonds can be formed in a chemical reaction,
existing bonds must be cleaved by high temp. or energetic radiation.

Distinction between:

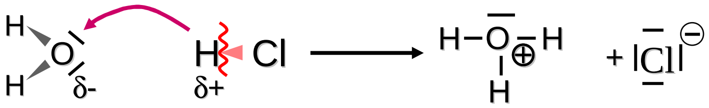
Homolysis: Cleavage of non-polar covalent bond into two radicals:

Radicals are atoms or molecules with a non-shared electron.
They are very energetic, have high reactivity and short lifetime.

Example: 

Initiation of chlorine/
hydrogen gas explosion

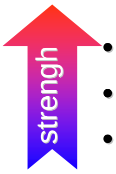
Heterolysis: Cleavage of a polar covalent bond into cation + anion:



Proton (H$^+$) transfer

2.3.4 Intermolecular (physical) Forces

Different attractive interactions can occur between
molecules, distinguished by strength and origin:

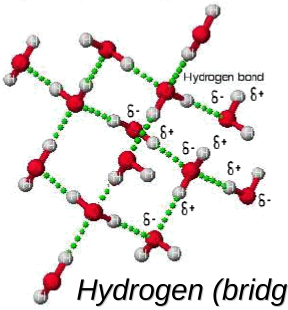


- Hydrogen-(bridge)-bonds: ≈ 10kJ/mol; by polar H
- Dipole-dipole interactions: ≈ 5kJ/mol by dipoles
- Van-der-Waals interactions: ≈ 1kJ/mol by all atoms

In contrast to *intramolecular* chemical (primary) bonds inside molecules, these *intermolecular* forces between molecules are physical (secondary) bonds.
At the boiling temperature the kinetic energy of the molecules exceeds the attractive forces.

Hydrogen Bonds

Hydrogen bond = attractive **interaction** of a **hydrogen atom** with an **electronegative atom** (N, O, F, ...) that comes from another molecule or chemical group. The hydrogen must be covalently bonded to another electronegative atom to create the bond.
These phys. bonds can occur between molecules (intermolecular), or within different parts of a larger single molecule (intramolecular).
This type of bond occurs in both inorganic molecules such as water and organic molecules such as proteins, cellulose or DNA



Hydrogen (bridge) bonds in water

molecule	molar mass	boiling temp.
CH_4	16 g/mol	-161 °C
NH_3	17 g/mol	-33 °C
H_2O	18 g/mol	100 °C

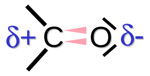
Boiling temperature is increased by hydrogen bonds

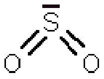
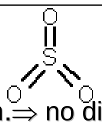
Dipole-Dipole Interactions

Dipole–dipole interactions = electrostatic interactions of permanent dipoles in molecules (asymmetrical polar bonds; e. g. H_2O, HCl, HF).
Attractive force between positive part of molecule and negative part of neighbored molecule

$\overset{\delta+}{H}—\overset{\delta-}{Cl}- - - - -\overset{\delta+}{H}—\overset{\delta-}{Cl}$

Polar atomic group without hydrogen: e. g. carbonyl group (org. chem.)

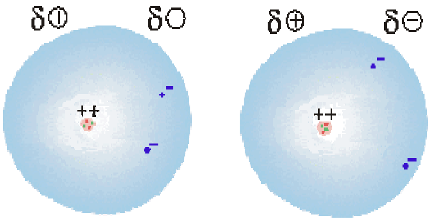


	 asym.⇒ dipole	 sym.⇒ no dipole
Melting temperature	17 °C	-76 °C
Boiling temperature	44 °C	-10 °C

Phase transition temperatures increases by dipolar interactions.

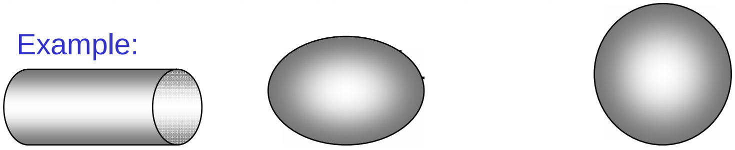
London Dispersion Forces (Van-der-Waals Interactions)

London dispersion forces (LDF) also called *Van-der-Waals forces* in the strict sense are weak intermolecular interactions arising from induced instantaneous polarization by random fluctuation of the electron density.



The LDF between molecules increases with surface:

Example:



n-pentane
old name: pentane

2-methyl butane
old name: iso-pentane

2,2-dimethyl propane
old name: neo-pentane

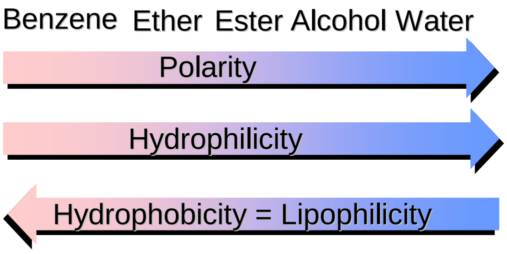
boiling T: 36℃ **28℃** **9,4℃**

Chemical Bonds and *Physical Bonds*
Summary

	Bond type Energy (kJ/mol)	positive charge	negative charge
chemical	Ionic bond Lattice enthalpy ≈1000	Cations	anions
	metallic bond	Cations	delocalized electrons (electron sea)
	Covalent bond ≈ 300 per bond	Nucleus	Electron shell
physical	Hydrogen bond ≈ 20 kJ/mol	H atom (polar bond to electronegative atom, N, O,)	Electronegative atom with lone-pair (O, Cl)
	Dipole-dipole ≈ 5 kJ/mol	permanently positively polarized atom in mol.	permanently positively polarized atom
	Van-der-Waals-bond ≈ 1 kJ/mol	instantaneously positively polarized atom	instantaneously positively polarized atom

Polar/non-polar Solvents hydrophilic/lipophilic

Several types of chemical reactions occur in solution, if a suitable solvent for the reactants can be found. The solubility depends on polarity of solvent and solute. The number, potency and arrangement of polar bonds in the molecule influences the polarity of the solvent:



Polar solutes or atomic groups are water soluble = ***hydrophilic***
Fats are non-polar and not water soluble (**hydrophobic**)
Non-polar compounds are ***lipophilic.***

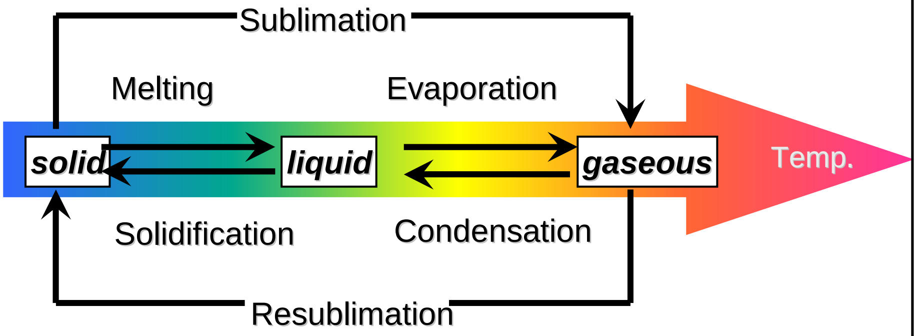
Ionic (Na^+Cl^-) or polar compounds (methanol) exhibit good solubility in water. Non-polar compounds (fat, oil, grease) are soluble in non-polar solvents (white spirit, ether, chloroform, etc.)

---

3. Physical Chemistry

Topics:
- State of matter/phase transitions
- Phase diagrams
- Homogeneous/heterogeneous systems
- Separation processes
- Thermodynamics
- Kinetics
- Chemical equilibrium

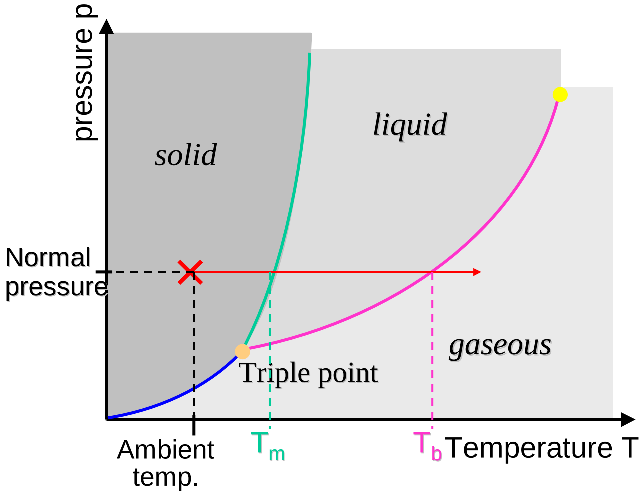
State of Matter
Phase Transitions; Separation



A **phase** is a region of space (in a thermodynamic system) throughout which all physical properties of a material are essentially uniform. States of matter are phases. The change of the state of matter is a phase transition.

The state of matter of a material or compound depends on ***temperature T*** ***and*** ***pressure p*** ⇒ p-t-phase diagram

Phase Diagram

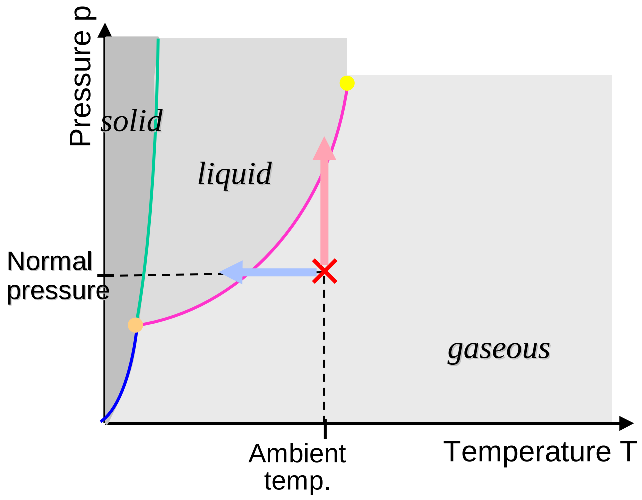


Position of melting curve, boiling curve and sublimation curve substance-specific.

Triple point: solid, liquid, and gaseous phase coexist.

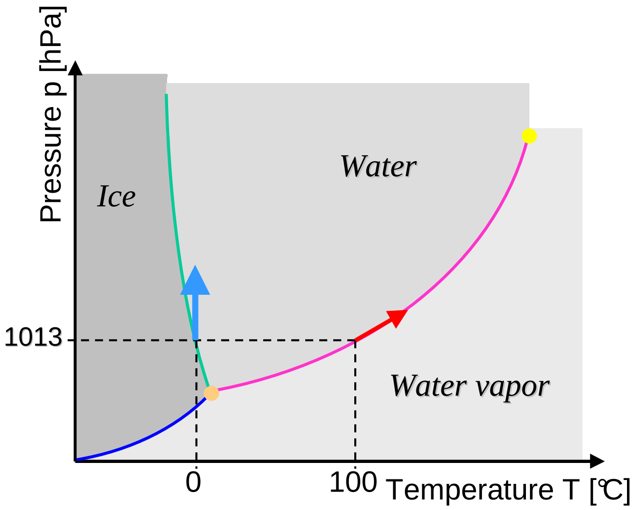
Example: Solid compound at normal conditions annealed until it melts (T_m) and evaporates (T_b)

Liquefaction of Gases



Gas can be liquefied by cooling or compression

Phase Diagram of Water



Anomaly:
Liquid water has a higher density than ice.
(Negative slope of melting curve)

Skating:
At const. low temperature (~ -5°C) pressure is increased
⇒ ice melts

Pressure cooker:
Higher pressure ⇒ higher boiling temp.
⇒ faster cooking

Multi Phase Systems heterogeneous Systems

heterogeneous Systems: Two or more ***components*** (= phases). Physical (and chemical) properties change instantaneously at **phase boundaries**.

Differentiation by combination of states of matter (Example)

(1) solid/solid	Mixture	(Granite = feldspar + quartz+ mica)
(2) solid/liquid	Suspension	(Blood = blood cells in blood plasma)
(3) liquid/liquid	Emulsion	(Milk = fat droplets in water)
(4) solid/gaseous	Smoke; foam	(cigarette smoke, Styrofoam)
(5) liquid/gaseous	Fog; foam	(Fog, whipped cream)
	= Aerosols	

Heterogeneous mixtures can of be separated into homogeneous (uniform) components by physical operations like filtration, centrifugation, decantation, etc.

Homogeneous Systems

In homogeneous systems the properties are uniform throughout the whole sample; no phase boundaries.
Homogeneous systems can be pure substances or multi component systems (=solutions).

Different types of solutions:

(1) solid/solid	(metal alloys, z. B. bronze)
(2) solid/liquid	(sugar dissolved in water)
(3) liquid/liquid	(alcohol + water)
(4) solid/gaseous	(solution of hydrogen in platinum)
(5) liquid/gaseous	(air dissolved in water)
(6) gaseous/gaseous	(air)

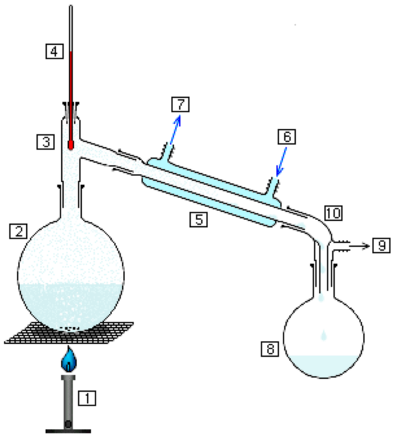
Homogeneous mixtures can also be separated into their components by physical operations, e. g.:

- Distillation: Separation by different boiling points; (distilling)
- Extraction: Separation by different solubility's; (coffee cooking)

Distillation

Thermal separation process: Mixture is separated into components by the differences in their boiling temperatures.
Mixture (2) is annealed (1); More volatile component (lower T_b) evaporates. Thermometer (4) indicates temperature of vapor (3) = boiling temperature.
In condenser (here Liebig cooler) (5) with cooling water plugs (6;7) the more volatile component condenses and drops into receiving flask (8).
Volume extension during evaporation ⇒ pressure equalization (9).
High boiling compounds bp.>200°C: low pressure (vacuum) distillation.
⇒ Lower boiling temperatures.

Examples: Essential Oils, pure alcohol, sea water ⇒ freshwater



The Chemical Reaction

A **chemical reaction** is a process that leads to the transformation of one set of chemical substances to another. Existing bonds between the atoms of the reactants (=reagents) are partly broken, new bonds are formed

Reaction equation: Reactant 1 (+ react. 2) $\longrightarrow$ product 1 + (product 2)

The connections among the atoms are altered, the number of atoms of the respective element remains constant.

During a chemical reaction the total mass of matter remains constant.

Law of conservation of mass

Antoine Lavoisier
fr. Chem. (1743-1794)

Chemical Thermodynamics
Chemical Kinetics

The electronic structure of the reactants (valency, polarity, etc.) indicate which chemical reactions are possible in general, but do they really take place and under which conditions? Sometimes side reactions can occur. Which product is formed?

Whether a chemical reaction takes place, to which extent and how fast is determined by the ***chem. thermodynamics*** and ***kinetics***.

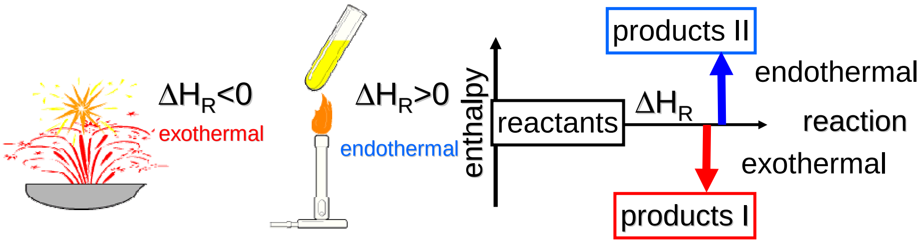
Chem. thermodynamics:
Under which conditions does a reaction occur spontaneously ?
Is heat released or consumed?
Chem. reactions always involve conversion of energy.
Whether a reaction occurs or not is related to the available chemical energy stored in the reactants and products.

Reaction kinetics: Study of rate of chemical reactions:
How much product is formed in time under given experimental conditions (e. g. concentration).

Reaction Enthalpy
Exothermal/Endothermal Reaction

Reaction enthalpy (ΔH_R) (= reaction heat) = how much heat is released or consumed during reaction.

Enthalpy negative $\Delta H_R<0 \Rightarrow$ heat released = **exothermal**
Enthalpy pos. ($\Delta H_R>0$) $\Rightarrow$ heating necessary = **endothermal**.

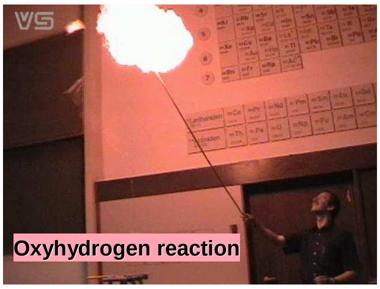


Chemical energy is stored in chemical compounds.
If the products (I) have lower energy state than reactants $\Rightarrow$ exothermal, energy released. (heat, light, bang)
If products (II) have higher energy content, reaction is endothermal, feed of energy required (heat, electricity).

Example for Exothermal/Endothermal Reaction

Example:

$$2\,H_2 + O_2 \underset{\text{Electrolysis}}{\overset{\text{Hydrogen-oxygen reaction}}{\rightleftarrows}} 2\,H_2O$$



H_2-O_2-reaction ΔH_R = - 286 kJ/mol (released; heat, light, bang)
During electrolysis of water ΔH_R = 286 kJ/mol
(consumed; electrical power)

Enthalpy of Formation Calculation of Standard Enthalpy of Reaction

The chemical internal energy = enthalpy H of a system cannot be measured directly. Change in enthalpy ΔH more useful quantity. By definition all elements have an enthalpy of zero.
Enthalpies are funct. of T und p ⇒ Standard cond. (25°C, 1 bar): H^0

Molar Enthalpy of Formation of a compound ΔH_f = amount of heat released or consumed during its formation from the elements.

Example: Molar standard enthalpy of formation of water:

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O\ (l) \qquad \Delta H_R = -286 \text{ kJ/mol}$$

$$\Delta H_f = 0 \qquad 0 \qquad -286 \text{ kJ/mol}$$

The reaction enthalpy can be calculated from the enthalpies of formation of involved compounds: $\boxed{\Delta H_R^0 = \sum \Delta H_f^0(products) - \sum \Delta H_f^0(reactants)}$

Example: Combustion of ethene:

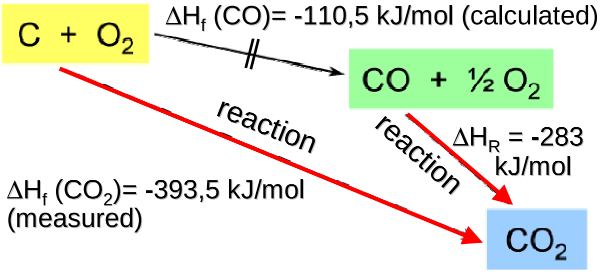
$$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O\ (g) \qquad \Delta H_R = -1322{,}9 \text{ kJ/mol}$$

$$\Delta H_f^0 = 52{,}3 \qquad 0 \qquad 2\cdot(-393{,}5) \qquad 2\cdot(-241{,}8) \text{ kJ/mol}$$

Hess Law

Hess: the enthalpy change for a reaction carried out in a series of steps is equal to the sum of the enthalpy changes for the individual steps

<u>Example</u>: ΔH_f CO not directly measurable, because CO_2 is formed too.



$C + O_2$

$\Delta H_f (CO) = -110,5$ kJ/mol (calculated)

$CO + ½ O_2$

reaction

reaction

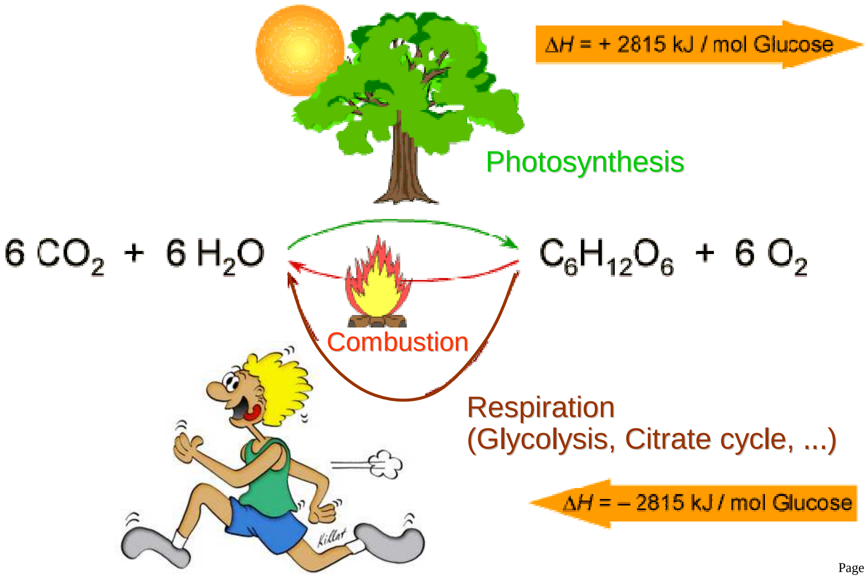
$\Delta H_R = -283$ kJ/mol

$\Delta H_f (CO_2) = -393,5$ kJ/mol (measured)

CO_2

$$\Delta H_f (CO) = \Delta H_f (CO_2) - \Delta H_R (CO \rightarrow CO_2)$$

Hess Law
and Biological Processes



$\Delta H = + 2815$ kJ / mol Glucose

Photosynthesis

$6\ CO_2 + 6\ H_2O$

$C_6H_{12}O_6 + 6\ O_2$

Combustion

Respiration
(Glycolysis, Citrate cycle, ...)

$\Delta H = - 2815$ kJ / mol Glucose

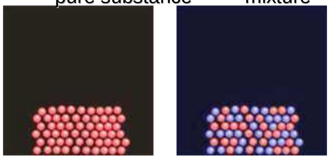
Entropy

Another thermodynamic property of matter is the **entropy**: Interpretation as molecular disorder or statistical number of possible arrangements.

$S_{solid} < S_{liquid} < S_{gas}$

solid liquid gas

$S_{pure\ substance} < S_{mixture}$



pure subst. mixture

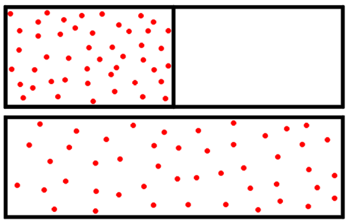
Change of Entropy

In closed thermodynamic systems, the entropy remains constant for completely reversible processes.
For irreversible processes the entropy increases.

Examples for irreversible processes with increase of entropy:

Heat exchange: 40 °C 40 °C

Diffusion:



Reaction entropy: $\Delta S_R^0 = \sum \Delta S^0(produkte) - \sum \Delta S^0(Edukte)$

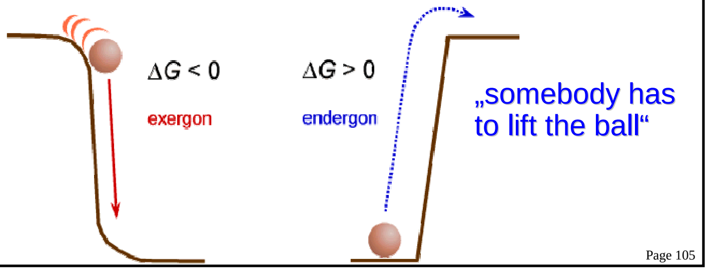
Gibbs (Free) Energy

The reactions enthalpy indicates, if process is exo- or endothermal, but not, if reaction occurs spontaneously. Endothermal spontaneous reactions can occur, which consume heat from the environment, which is cooled.

Driving force for a reaction is the ***Gibbs (Free) Energy*** ΔG.

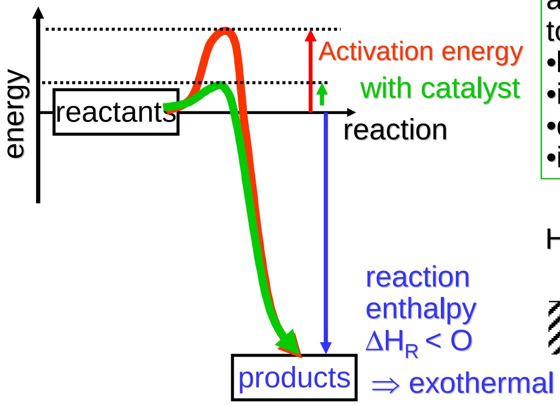
Gibbs-Helmholtz equation: $\Delta G = \Delta H - T \cdot \Delta S$

Reactions occur spontaneously, if $\Delta G < 0$ (exergonic reaction).
If $\Delta G > 0 \Rightarrow$ endergonic reaction, absorbs energy from surrounding.

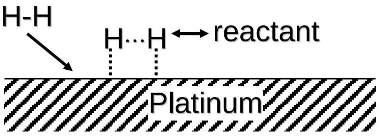


Activation Energy
Catalysis

The activation energy is the minimum energy required to start a chemical reaction („igniting spark“) (cleavage of existing bonds), even for exothermal reactions in which the released heat exceeds the activation energy by far.



A ***catalyst*** (chem. compound added in small amounts to reaction)
- lowers activation energy,
- increases reaction rate
- doesn't influence equilibrium
- is not consumed by reaction



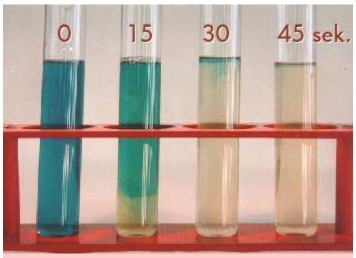
Kinetics

Reaction kinetics: Speed of chemical reactions.
Reaction rate defined as change of concentration with time

For a reaction: A + B → P: $r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[P]}{dt}$

i.e.: increase of concentration of product P
resp. decrease of reactant A or B with time.

Monitoring progress of reaction by
- change of color
- spectroscopic
- conductometric
- calorimetric (heat measurement)



reduction of methylene blue by glucose

Rate Law
Reaction Order

The reaction rate depends on the concentration of the involved compounds ⇒ **rate law**:

For A + B → P: $\boxed{r = -\frac{d[A]}{dt} = k(T) \cdot [A]^a \cdot [B]^b}$

The order of reaction is defined as the sum of all the exponents of the reactants involved in the rate equation.
k is the **rate constant,** which is temperature dependent as a rule.

reaction	order	rate law
A → P	1. order	-d[A]/dt = k·[A]
A + B → P	2. order	-d[A]/dt = k·[A]·[B]

Chemical Equilibrium
Reversible/Irreversible Reaction

In general, a chemical reaction can be reversed:
The products can react with each other to form the original reactants.
Such a reaction is called a **reversible** reaction.

Reversible reaction: $A + B \rightleftharpoons C + D$

Forward and reversed reaction occur simultaneously so that a **dynamic equilibrium** is formed, in which A and B react continuously to C und D, while C and D form A and B again. Once the equilibrium is reached, the net concentrations remain constant.

A reaction without reversed reaction is called **irreversible**.
It occurs until A and/or B are consumed completely or, if C and/or D are removed from the reaction site.

Irreversible reaction: $A + B \longrightarrow C + D$

Law of Mass Action

The equilibrium state of a chemical reaction can be described quantitatively by the **Law of Mass Action** (Guldberg/Waage 1865).

$$A + B \rightleftharpoons C + D \quad \textit{Equilibrium constant} \quad k_c = \frac{k_{\leftarrow}}{k_{\rightarrow}} = \frac{c(C) \cdot c(D)}{c(A) \cdot c(B)}$$

Concentrations are multiplied! By convention product ⇒ numerator

in general: $aA + bB \Leftrightarrow cC + dD$ $\qquad k_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$

Almost complete reaction: $A + B \overset{\longrightarrow}{\leftarrow} C + D$ $\quad k_c$>>1 ; z.B. 10^{12}

Equivalent equilibrium: $A + B \rightleftarrows C + D$ $\quad k_c$=1

Barely occurring reaction: $A + B \overset{\rightarrow}{\longleftarrow} C + D$ $\quad k_c$<<1 ; z.B. 10^{-12}

Application of Law of Mass Action:
- Solubility of salts
- Autoprotolysis of water

Le Chatelier´s Principle

Change of concentration:
Changing the concentration of an ingredient (C) will shift the equilibrium to the side that would reduce the change. By the reversed reaction C and D are consumed partly, while the concentration of A and B is increased until k_C reached.

$$A+B \rightleftarrows C+D$$

$$A+B \leftarrow \mathbf{C}+D$$

$$A+B \rightleftarrows C+ {\scriptstyle D}$$

$$k_c = \frac{[C]\cdot[D]}{[A]\cdot[B]}$$

$$A + B \rightleftarrows C + D + Energy$$

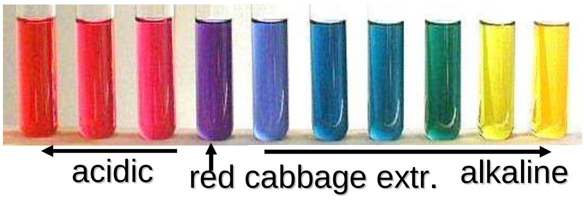
Change of temperature.:
Exothermal reaction has energy (heat) as product. Cooling removes heat and the equilibrium is shifted to the product side.
Endothermal reactions are enhanced by feeding energy.

Change of pressure/volume: In reactions with volume decrease (compression) increasing pressure shifts the equilibrium to product side.

Example: $N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$ $\quad A + B + P\,/V \rightleftarrows C + D$

4. Inorganic Chemistry
4.1 Acids – Bases

Historically, acids are compounds, which taste sour (vinegar, lemon). Those compounds change the color of certain vegetal ingredients to red (red cabbage; litmus). (R. Boyle, 1663)



Substances, which taste and feel soapy, were called ***alkalis*** *(arab.:Plant ash←Potassium hydroxide)*. ***Lye*** = corrosive alkaline substance. Later such chemicals were called ***bases***, since they are (together with an acid) the base for formation of salts.

Bases can change the color of certain plant ingredients, too.

Lavoisier (~1770) assumed, that acids contain oxygen, because non-metal oxide (e. g. CO_2) together with water form acids.

Observation: (Hydrochloric) acid dissolves lime ($CaCO_3$) and zinc involving gas development. It does not react with copper.

Acid Rain

The source of acid rain are the oxides of carbon, nitrogen and sulfur, which are formed by the combustion of fossil fuels (coal, mineral oil, natural gas) They react with water molecules to produce acids.

Carbon dioxide:

- $CO_2 + H_2O \rightarrow H_2CO_3$

Nitroxides:

- $2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

Sulfur oxides:

- $SO_2 + H_2O \rightarrow H_2SO_3$
- $SO_3 + H_2O \rightarrow H_2SO_4$

The produced acids are harmful for plants, waters, and buildings:

1908 1968
limestone sculptures in industr. area

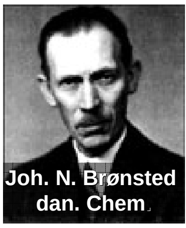
$$\underset{\text{solid}}{CaCO_3} + 2H_2SO_4 \rightarrow \underset{\text{gaseous}}{CO_2} + H_2O + \underset{\text{soluble}}{Ca^{2+} + SO_4^{2-}}$$

Acid-Base Theory by Brønsted

Comprehensive acid-base theory by ***Brønsted*** *(1923):*

Acids: Proton donators; compounds or specimens, that release protons.

Bases:Proton acceptors; compounds or specimens, that absorbs (gains) protons.



Joh. N. Brønsted
dan. Chem.

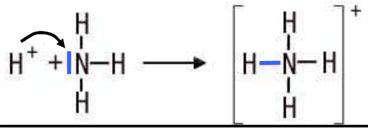
Advantage: Definition is

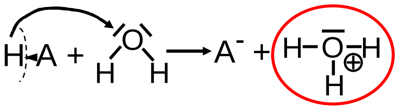
- independent of water as solvent
- not restricted to liquid phase ⇒
- more bases, e. g. ammonia (NH_3)

$HCl\ (g) + NaOH\ (s) \rightarrow Na^+Cl^-(s) + H_2O\ (l)$

Bases must have a lone pair to receive a proton

In water Brønsted acids produce hydronium ions:





Dissociation Equilibrium
Conjugate Acid/Base

If an acid HA reacts with a base B, a proton is transferred from the acid to the base (***protolysis***).

			conjugate	
acid	**base**		**acid**	**base**
HA	+ B	$\rightleftharpoons$	HB^+	+ A^-
CH_3COOH	+ NH_3	$\rightleftharpoons$	NH_4^+	+ CH_3COO^-
S_1	+ B_2	$\rightleftharpoons$	S_2	+ B_1

In the reversed reaction, a proton is transferred from HB^+ to A^- i. e., HB^+ acts as acid, A^- as base.

In such a ***dissociation equilibrium*** two sets of acid-base pairs occur: S_1/B_1 and S_2/B_2.
A^- is called ***conjugate*** base to HA
and HB^+ conjugate acid to B.

Acid and bases can be neutral molecules or ions.

Example: Acetic acid + ammonia → ammonium- + acetate ion

Ampholyte

An **ampholyte** molecule (or ion) can either donate or accept a proton, thus acting either as an acid or a base.

Example:
Water reacts toward nitric acid as a base: It receives a proton and becomes a hydronium ion.
Towards the base ammonia water reacts as an acid, however, releasing a proton and becoming a hydroxide ion.

$$H_2O + HNO_3 \rightarrow H_3O^+ + NO_3^-$$

$$H_2O + NH_3 \rightarrow OH^- + NH_4^+$$

More ampholytes:
HCO_3^- (Hydrogen carbonate ion), HSO_4^- (Hydrogen sulfate ion)

Acid/base designates a **chemical behavior** towards a reaction partner, rather than a class of substance.
Names (e .g. nitric acid) are historical regarding reaction with water.

Acid-Base Theory by Lewis

1927; G.N. Lewis: Even more general def. for acids and bases:
(independent of protons or hydroxide ions)

Lewis-acid: Specimen, with empty outer orbital, ready to receive electron pair; has electron pair gap (does not comply with octet rule!)

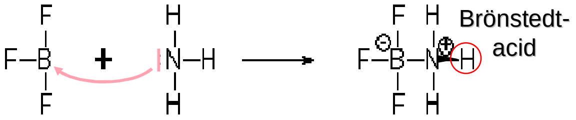
Lewis-acid: Electron pair acceptor

Lewis-base has a free electron pair, which can add to a Lewis acid to form a new electron pair bond.

Lewis-base: Electron pair donator

Example:

New bond by overlap of empty boron orbital with occupied nitrogen orbital



Lewis acid Lewis base Lewis acid-base aduct

General Structure of Acids

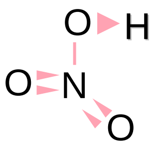
What is the general structure of a *Brønsted acid?*
Brønsted acids contain polar bonded hydrogen.

Which elements form polar bonds with H ?
Non-metals (electronegative!) form polar bonds with H.

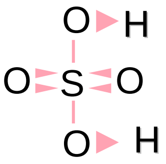
Example: Hydrogen chloride H◄Cl other halogens analogous

Elements with lower electronegativity (S,N,P,C) can increase polarity by additional bonds to oxygen atoms:

Examples: Nitric acid



Sulfuric acid



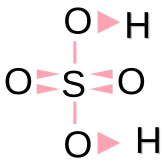
Citric acid

Strong/Weak Acids/Bases

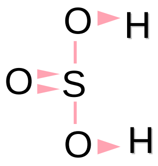
Acids and bases are graded **strong** or **weak** regarding their tendency to release resp. receive protons.

The more polar the hydrogen is bonded, the greater the tendency for dissociation = protolysis, the stronger the acid.

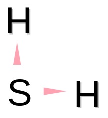
Examples: Sulfuric acid Sulfurous acid Hydrogen sulfide



is stronger acid than:



is stronger acid than:



Strong acids (HCl, H_2SO_4, HNO_3, H_3PO_4, $HClO_4$) dissociate in water almost **completely**: $HA + H_2O \rightarrow H_3O^+ + A^-$

Strong acids have weak conjugate bases;
strong bases have weak conjugate acids.

Polyacids

Some acids can release more than one proton via different protolysis steps. The second step is hampered compared to the first.
Example: two-proton acid carbonic acid (H_2CO_3).

conjugate acid-base-pairs

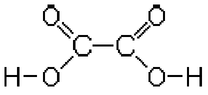
$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$ 1. step H_2CO_3 / HCO_3^- und H_3O^+ / H_2O

$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$ 2. step HCO_3^- / CO_3^{2-} und H_3O^+ / H_2O

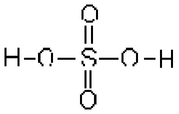
Intermediate (e. g. hydrogen carbonate ion) = ampholyte !

More poly-acids:

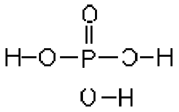
Oxalic acid $H_2C_2O_4$



Sulfuric acid H_2SO_4



Phosphoric acid H_3PO_4



Concentrate/Dilute Strong Acids
Molarity

Mixing of pure, concentrate acid with water ⇒ **dilute acid**.

Warning: During dilution of concentrate acids (in particular sulfuric acid) with water large amounts of heat are released;, rapid evaporation of water; uncontrolled spray of acidic liquid
Rule: Add acid slowly to water – never add water to conc. acid!

Concentration c (= ***Molarity M*** (outdated but still common)) of acid/base
= Number of Mole dissolved acid/base in 1 L.
M > 1 mol/L ⇒ conc. acid; M < 1 mol/L ⇒ dilute acid

Example: conc. (69%mass) nitric acid has density $\rho=1{,}41\ g/cm^3$
1 L⇔1410g; 69%⇔973g pure HNO_3; molar mass=63 g/mol;
n=m/M = 973g/63g/mol=15,4 mol ⇒conc. nitric acid = 15,4 M HNO_3

How much conc. acid for 100 ml of 0,1 M (dilute) HNO_3 ?
$n = V\cdot c = 0{,}01\ mol\ HNO_3$

$$\frac{1000ml}{15{,}4mol}=\frac{x}{0{,}01mol}\Rightarrow x=0{,}65ml \Leftrightarrow \mathit{0{,}92g}$$

Strong Acids

Sulfuric acid: Made from sulfur trioxide (SO_3) + $H_2O \rightarrow H_2SO_4$
100%: $\rho=1{,}8\ g/cm^3$; 1800g/98g/mol = 18 mol/L = 18 M H_2SO_4
additional phys. solution of SO_3 ⇒ Oleum (hygroscopic)

Hydrochloric acid = aqueous solution of hydrochloric gas $(HCl)_{(g)}$;
max. 40 % ⇒13 mol/L hydrochloric acid
Complete dissociation: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$
> 36% = fuming acid. ⇐ HCl gas evaporates

Nitric acid = HNO_3 ; concentrate = fuming 90% HNO_3
⇒ free NO_2 (brown toxic gas);
dissolves silver, but not gold (aqua fortis)

Nitrating acid: Mixture of nitric + sulfuric acid for nitration of compounds; e g. toluene ⇒ trinitrotoluene (TNT)

Aqua Regia = HCl/HNO_3 (3:1) dissolves gold

Common Acids and their Conjugate Bases

Hydrochloric acid	$HCl_{(aq)}$	Chloride ion	Cl^-		
Hydrofluoric acid	HF	Fluoride ion	F^-		
Sulfuric acid	H_2SO_4	Hydrogen sulfate	HSO_4^-	Sulfate	SO_4^{2-}
Sulfurous acid	H_2SO_3	Hydrogen sulfite	HSO_3^-	Sulfite	SO_3^{2-}
Nitric acid	HNO_3	Nitrate ion	NO_3^-		
Nitrous acid	HNO_2	Nitrite ion	NO_2^-		
Phosphoric acid	H_3PO_4	Dihydrogen phosphate Hydrogen phosphate	$H_2PO_4^-$ HPO_4^{2-}	Phosphate	PO_4^{3-}
Carbonic acid	H_2CO_3	Hydrogen carbonate	HCO_3^-	Carbonate	CO_3^{2-}
Perchloric acid	$HClO_4$	Perchlorate ion	ClO_4^-		
Hydrogen cyanide	HCN	Cyanide ion	CN^-		
Acetic acid	CH_3COOH	Acetate ion	CH_3COO^-		

Ampholytes

Common Bases/Alkalis

Caustic soda = alkaline solution of sodium hydroxide (NaOH) in water; max. 1200 g = 30 mol/L
exothermal process!
Production: Electrolysis of alkali chlorides
(see: *Industrial Chemistry*)

Potash lye = alkaline solution of potassium hydroxide (KOH) in water; exothermal process!

Ammonia water = Ammonium hydroxide = Sal ammoniac
Ammonia (gas) dissolved in water: $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

Carbonic Acid

Gaseous carbon dioxide soluble in water: $(CO_2)_{(g)} \rightleftharpoons (CO_2)_{(aq)}$.

partly reacts to carbonic acid: $CO_{2\ (aq)} + H_2O \rightleftharpoons H_2CO_3$

Carbonic acid is a weak acid, dissociates only partly forming hydrogen carbonate ions (Ampholyt). $H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$

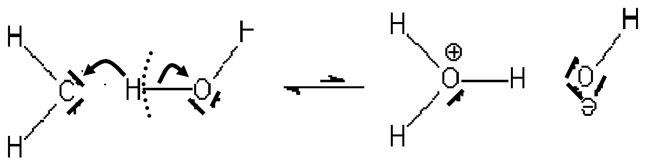
In a second protolysis step carbonate ions can be produced: $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$

In carbonated water all species coexist in a chemical equilibrium in different concentrations. Addition of lemon (acid, H_3O^+) shifts all equilibriums to the left ⇒ more CO_2 gas escapes.

Autoprotolysis of Waters

Salt solution are electrical conductive, since they contain ions.
Application of voltage ⇒ ions are moved: $Cat^+ \rightarrow$ cathode (neg. pole)
: $An^- \rightarrow$ anode (pos. pole)

Pure, distilled water is conductive too,
because water always contains ions due to ***autoprotolysis***:



$H_2O + H_2O \rightleftharpoons [H_3O]^+ + [OH]^-$

Water acts as acid **and** as base,
hydronium ions and hydroxide ions are produced
in small concentrations.

Ion(ic) Product of Water

$$K = \frac{[H_3O^+]\,[OH^-]}{[H_2O]\,[H_2O]}$$

Law of mass action
for autoprotolysis

$$K\,[H_2O]^2 = K_W = [H_3O^+]\,[OH^-]$$

Derivation of ion product of water
from law of mass action

$$K_W = c(H_3O^+)\cdot c(OH^-) = 10^{-7}\frac{mol}{L}\cdot 10^{-7}\frac{mol}{L} = 10^{-14}\frac{mol^2}{L^2}$$

The ion product of aqueous solutions is **always** 10^{-14} mol²/L²

By addition of hydronium ion (from acid) shifts the equilibrium, H_3O^+ and OH^- react until K_W $=10^{-14}$ again. Now, $[H_3O^+]>10^{-7}$ and $[OH-]< 10^{-7}$

$$H_2O + H_2O \rightleftarrows [H_3O]^+ + [OH]^-$$

$$H_2O + H_2O \xleftarrow{\;\rightarrow\;} \mathbf{[H_3O]^+} + [OH]^-$$

$$H_2O + H_2O \rightleftarrows [H_3O]^+ + [OH]^-$$

The pH Value

The concentration of hydronium ions is a measure for acidic or alkaline character of a solution.
Representation as decimal number confusing
in powers of 10 inconvenient, therefore definition:

The pH value is the negative decimal logarithm of the hydronium ion concentration. (**p**otentia **h**ydrogenii)

$$\boxed{pH = -\lg[c(H_3O^+)]}$$

$c(H_3O^+)$ mol/L decimal	$c(H_3O^+)$ mol/L power	pH value	solution
1	10^0	0	very acidic
0.0001	10^{-4}	4	moderate acidic
0.0000001	10^{-7}	7	neutral
0.0000000001	10^{-10}	10	moderate alkaline
0.00000000000001	10^{-14}	14	very alkaline

Relationship between Hydronium and Hydroxide Ion Concentration

In neutral water is: $c(H_3O^+) = c(OH^-) = 10^{-7}$ mol/L

For **every** solution is: $c(H_3O^+) \cdot c(OH^-) = 10^{-14}$ mol²/L²
Note: concentrations are multiplied!

Analogous to pH a pOH value can be defined:

The pOH value is the negative decimal logarithm of the hydroxide ion concentration.

$$pOH = -\log[c(OH^-)]$$

$c(H_3O^+) \cdot c(OH^-) = 10^{-14}$ mol/L logarithm ⇒ $\boxed{pH + pOH = 14}$

Examples:

pH	pOH	solution
2	12	acidic
7	7	neutral
11	3	alkaline

pH calculation

(strong acid or strong base)

Example:

n =0,1mol of strong acid (HA) added to V=10 L water. pH = ?

$HA + H_2O \rightarrow H_3O^+ + A^-$ (1 mol acid produces 1 mol hydronium)

$$c(H_3O^+) = n_{HA}/V = 0{,}1 mol/10 L = 0{,}01 mol/L = 10^{-2} mol/L$$

$$pH = -\log[c(H_3O^+)] = -\log 10^{-2} = 2$$

Example:

0,01 mol of strong base added to 100 L of water. pH = ?

$$c(OH^-) = n_B/V = 0{,}01 mol/100 L = 0{,}0001 mol/L = 10^{-4} mol/L$$

$$pOH = -\log[c(OH^-)] = -\log 10^{-4} = 4$$

$$pH = 14 - pOH = 14 - 4 = 10$$

pH Values of Common Solutions

Substance	pH-Wert	Art
Battery acid	-0,5	Acidic
Gastric acid	2,0	
Lemon juice	2,4	
Coke	2-3	
	2,7	
Vinegar	2,9	
Orange/apple juice	3,5	
Wine	4,0	
Sour milk	4,5	
Beer	4,5 – 5,0	
Acid rain	<5,0	
Coffee	5,0	
Tee	5,5	
Rain	5,6	
Mineral water	6,0	
Milk	6,5	
Distilled water	7,0	Neutral

Substance	pH-Wert	Art
Saliva	6,5 – 7,4	Acidic to
Blood	7,34 – 7,45	Alkaline
Sea water (today)	8,05	
Sea water (pre-industrial)	8,16	
Intestine	8,3	
Soap	9,0 – 10,0	
Sal ammoniac	11,5	
Bleaching agent	12,5	
Concrete	12,6	
Caustic Soda	13,5	

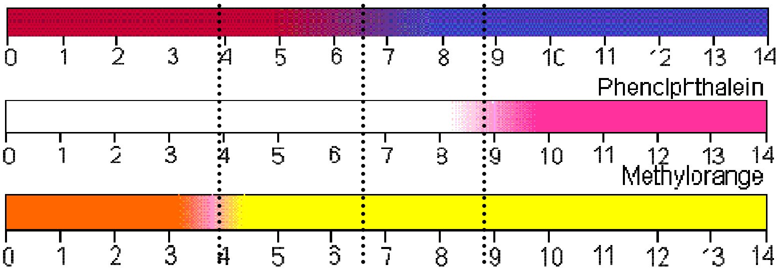
pH Indicator

A **pH indicator** is a halochromic compound added in small amounts to a solution to visualized acidity resp. basicity by color.

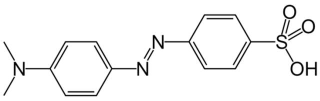
Indicators are colored compounds, which undergo acid-base-reactions ⇒ chemical structure and color is changed.

Indicator enable a rough determination of the pH value:

Examples:



Chemical structure of the indicator methyl orange



pH Test Strip/pH Meter

pH Test strips contain a mixture of different indicators. Comparison of color with reference scale ⇒ pH value.

In a pH-Meter electrochemical determination of H_3O^+ ion concentration and calculated pH value displayed.

Neutralization

Combination of an acidic solution with a certain with a certain $c(H_3O^+)$ with an identical volume of an alkaline solution with the same $c(OH^-)$ produces a neutral solution (pH=7).
The underlying reaction is a ***neutralization***.

$$H_3O^+ + OH^- \longrightarrow H_2O + H_2O$$

If identical amounts of substance (equimolar amounts) of H_3O^+ and OH^- are combined, they react in a neutralization reaction to neutral water.

Attributes of a neutralization:

- represents an acid-base-reaction, proton transfer H_3O^+ to OH^-.
- exothermal reaction; reaction heat is released!
- used in quantitative analysis for determination of unknown $c(H_3O^+)$ or $c(OH^-)$: Acid-base titration (later)

Calculation of Neutralization Reaction

In a submarine 180 L acid are leaked out of the battery cells with pH = 1. How much sodium hydroxide solution of c = 2 mol/L is necessary for a complete neutralization (pH = 7) ?

Neutralization means:
amount of substance of acid (H_3O^+)
is equal to amount of base (OH^-)

$$n_A = n_B$$

$$c_A \cdot V_A = c_B \cdot V_B \qquad c_A = 10^{-pH} = 0{,}1\ mol/L$$

$$V_B = c_A \cdot V_A / c_B$$

$$V_B = \frac{0{,}1 mol/L \cdot 180L}{2mol/L} = 9L$$

Formation of Salt by Neutralization

In addition to H_3O^+ and OH^- -ions acidic and alkaline solutions both contain counter ions (electric neutrality).
They can be product of a previous acid-base-reaction from production of the acidic solution:

Example: $HCl\ (g) + H_2O\ (l) \rightarrow Cl^-\ (aq) + H_3O^+\ (aq)$

or they result from the dissolution of a compound in water:

Example: $NaOH\ (s) \xrightarrow{H_2O\ (l)} Na^+\ (aq) + OH^-\ (aq)$

Total reaction of the neutralization:

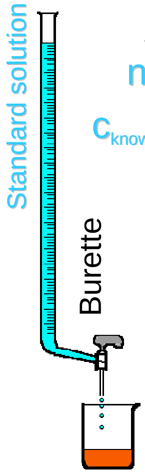
$Cl^-_{(aq)} + H_3O^+_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)} + 2H_2O$

If the water is evaporated NaCl (table salt) is remaining.

Acid + Base → Salt (+ Water)

Quantitative Analysis
Titration

Determination of the concentration of an unknown solution by defined addition of another solution (standard solution with known conc.) until equivalence point is reached, visualized by indicator.



At equivalence point:

$$n_{known} = n_{unknown}$$

$$c_{known} \cdot V_{known} = c_{unknown} \cdot V_{unknown}$$

$$c_{unknown} = \frac{c_{known} \cdot V_{added}}{V_{receiving}}$$

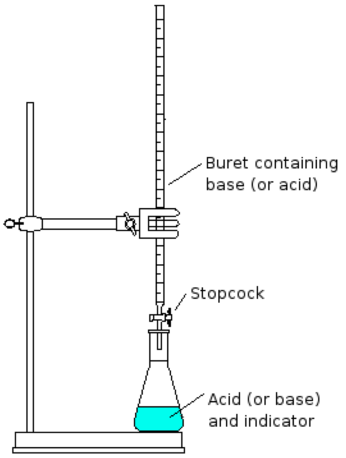
unknown solution

Reaction has to be:
- complete
- known stoichiometry
- fast
- End point detectable

Suitable reactions:
- Neutralization
- Redox reaction
- (Complexation)

Acid-Base-Titration
(Principle)

Acidic solution, $c(H_3O^+) = ?$ Measuring a certain volume of acid V_A; Drop wise addition of sodium hydroxide solution with known concentration c_B until pH=7 (neutralization); Measuring the consumption of basic solution V_B.



At equivalence point:

$$n_A \cdot (z_A) = n_B$$

with number of acid protons z_A

with $n = c \cdot V$

$$c_A \cdot V_A \cdot (z_A) = c_B \cdot V_B \qquad c_A = c_B \cdot \frac{V_B}{V_A \cdot (z_A)}$$

Quantitative Acid-Base-Reaction (Strong Acid/Base)

If a certain amount of base is added to an existing acidic solution, the acid is neutralized partly.
What is the concentration of the remaining acid ?;
Which pH-value is reached ?

In the existing acid with a volume V_A and a concentration c_A the amount of H_3O^+ is:

$$n_{0(H_3O^+)} = c_A \cdot V_A \cdot z_A$$

The addition of base produces a certain amount of OH^- ions:

$$n_{(OH^-)} = c_B \cdot V_B$$

Part of the H_3O^+ is neutralized; the remaining amout is:

$n_{(H_3O^+)} = n_{0(H_3O^+)} - n_{(OH^-)}$ with the conc.: $c_{(H_3O^+)} = \dfrac{c_A \cdot V_A \cdot z_A - c_B \cdot V_B}{V_S + V_B}$

Volumes have to be added

For identical conc. $c_A=c_B$ und $z_A=1$, simple equation:

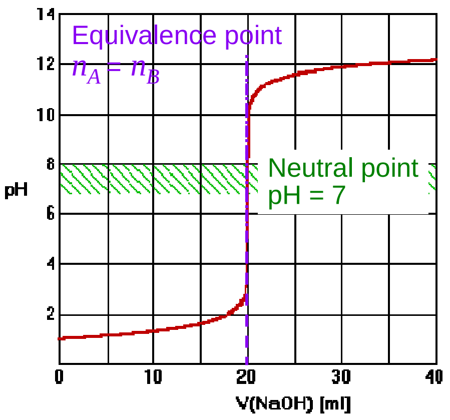
$$\boxed{c_{(H_3O^+)} = \frac{c \cdot (V_A - V_B)}{V_A + V_B}}$$

Titration Curve (Strong Acid/Strong Base)

Titration of 20 ml 0.1 molar HCl with 0.1 M NaOH ($c_A=c_B$, $z_A=1$)

$$\boxed{c_{(H_3O^+)} = \frac{0{,}1 \cdot (20 - V_B)}{20 + V_B}}$$

Addition V_B NaOH [ml]	c(H_3O^+) mol/L c(OH^-) mol/L	pH value
0	0,1	1
5	0,06	1,22
10	0,033	1,47
15	0,014	1,84
19	0,0025	2,6
19,9	$2{,}5 \cdot 10^{-4}$	3,6
19,99	$2{,}5 \cdot 10^{-5}$	4,6
20	10^{-7}	7*
21	0,0025	11,4
30	0,02	12,3
40		12,5



* Ion product of water relevant

$$\boxed{c_{(OH^-)} = \frac{0{,}1 \cdot (V_B - 20)}{20 + V_B}}$$

Acidity Constant;
pK_A Value

In addition to very strong acids, which dissociate completely, weaker acids exist, which dissociate only partly.
Their equilibrium reaction in water is described by the law of mass action.

$$HA + H_2O \leftrightarrows H_3O^+ + A^-$$

$$K = \frac{c(H_3O^+) \cdot c(A^-)}{c(HA) \cdot c(H_2O)} \quad \text{since } c(H_2O) \approx \text{const.} \Rightarrow \quad K_A = \frac{c(H_3O^+) \cdot c(A^-)}{c(HA)}$$

The ***acidity constant K_S*** is a measure for the strength of the acid

Often, the negative decimal logarithm ***pK_A*** is represented:

$$pK_A = -\log K_A$$ Analogous K_B and pK_B for bases

Important note: ***pH*** describes ***individual solution property***
In contrast to: ***pK_A*** describes ***compound property!***

---

pK_A Table

very strong
strong
weak

acid	Name	conjugated base	pK_A
$HClO_4$	Perchloric acid	ClO_4^-	-9
HCl	Hydrochloric acid	Cl^-	-6
H_2SO_4	Sulfuric acid	HSO_4^-	-3
H_3O^+	Hydronium ion	H_2O	-1,74
HNO_3	Nitric acid	NO_3^-	-1,32
$HClO_3$	Chloric acid	ClO_3^-	0
HSO_4^-	Hydrogen sulfate	SO_4^{2-}	1,93
H_3PO_4	Phosphoric acid	$H_2PO_4^-$	1,96
HF	Hydrofluoric acid	F^-	3,14
CH_3COOH	Acetic acid	CH_3COO^-	4,75
(H_2CO_3)	Carbonic acid	HCO_3^-	6,46

acid	Name	conjugated base	pK_A
H_2S	Hydrogen sulfide	HS^-	7,06
$H_2PO_4^-$	Dihydrogenphosph.	HPO_4^{2-}	7,21
$HClO$	Hypochloric acid	ClO^-	7,25
NH_4^+	Ammonium ion	NH_3	9,21
HCO_3^-	Hydrogencarbonate	CO_3^{2-}	10,4
H_2O_2	Hydrogen peroxide	HO_2^-	11,62
HPO_4^{2-}	Hydrogenphosphate	PO_4^{3-}	12,32
HS^-	Hydrogensulfid-ion	S^{2-}	12,9
H_2O	water	OH^-	15,74
OH^-	hydroxide-ion	O^{2-}	24

weak
moderate
strong

For conjugated acid-base pairs is: $pK_A + pK_B = 14$

Degree of Protolysis
(Degree of Dissociation)

Degree of protolysis α = Fraction of dissociated acid in equilibrium.

$$\alpha = \frac{\text{concentration of dissociated acid}}{\text{total concentration of acid}} = \frac{c(HA)_0 - c(HA)}{c(HA)_0}$$

Degree of protolysis depends on K_A value (resp. pK_A)
and on initial concentration of acid c_0:

Ostwald Law of Dilution: $$\alpha = \sqrt{K_A / c_0}$$

Stronger acid **or**
lower concentration
⇒ more dissociation
(=protolysis)

pH Calculation II
(Weak Acid)

$$K_A = \frac{c(H_3O^+) \cdot c(A^-)}{c(HA)}$$

since $c(H_3O)^+ = c(A^-)$
and weak acid ⇒
little dissociation: $c(HA) \approx c(HA)_0$

$$K_A = \frac{c(H_3O^+)^2}{c(HA)_0} \quad \Rightarrow \quad c(H_3O^+) = \sqrt{K_A \cdot c(HA)_0}$$

logarithm ⇒ $$pH = \tfrac{1}{2}[pK_A - \log c(HA)_0]$$

Example:
0,1 mol acetic acid (pK_A = 4,75) in 1 L water:

$$pH = \tfrac{1}{2}[4{,}75 - \log 0{,}1] = \tfrac{1}{2}(4{,}75 + 1) = 2{,}875$$

Buffer Solutions

Buffer solutions contain a weak acid ***and*** its conjugate weak base together.
Buffers stabilize the pH value against external acid/base attack.
Only minor changes of pH by addition of acid or base.

$$K_A = \frac{c(H_3O^+)\cdot c(A^-)}{c(HA)} \quad \Rightarrow \quad c(H_3O^+) = K_A \cdot \frac{c(HA)}{c(A^-)}$$

take logarithm ⇒ $$pH = pK_A + \log\frac{c(A^-)}{c(HA)}$$

Henderson-Hasselbalch equation:
Calculation of pH of buffer solution

For pH < pK_A, more acid than conjugate base;
for pH > pK_A, more conjugate base than acid.

Buffer Effect

Buffer solution neutralizes added strong acid or base partly, by shifting the equilibrium.

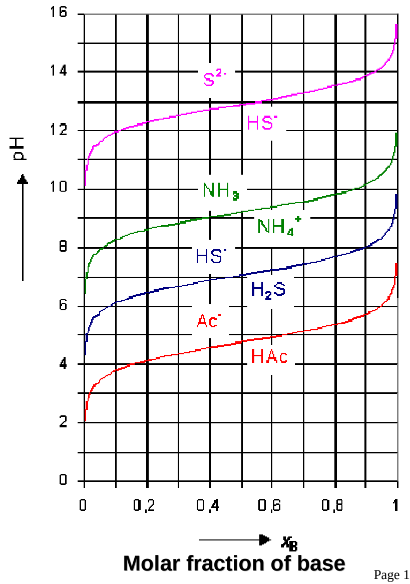
Most effective buffer,
if c(HA):c(A^-) = 1:1
(so that pH = pK_A)

Strong acid (H_3O^+) is converted into weak acid

$$H_3O^+ + A^- \rightarrow HA + H_2O$$

Buffering of base analogous

Excess of acid or base by
a factor of 10 alters
the pH value only by 1!



Titration Curve
Weak Acid/Strong Base

Example:
20 ml 0.1 molar acetic acid (pK_A=4,75); 0.1 M NaOH added

Initially:

$$pH = \tfrac{1}{2}[4{,}75 - \log 0{,}1] = 2{,}875$$

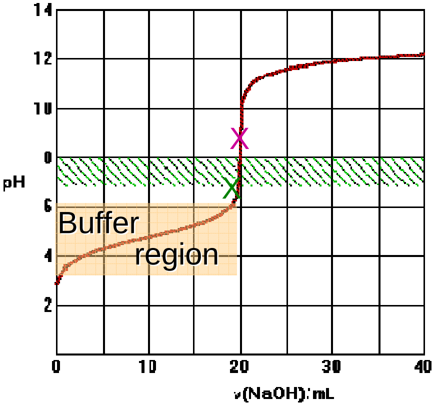
By addition of NaOH solution:
$HAc + OH^- \rightarrow Ac^- + H_2O$

HAc/Ac- Buffer: $pH = 4{,}75 + \log \frac{c(Ac^-)}{c(HAc)}$

Addition NaOH [ml]	pH-Wert
0	2,875
5	4,27
10	4,75
19	6
19,86	7
20	8,72

>25 as for HCl/NaOH

Neutral point:pH = 7<Equivalence pH=8,72



Equivalence p.: all HAc neutralized; only 0,05 mol/L Ac^- (pK_B = 9,25)

$$pH = 14 - \tfrac{1}{2}[9{,}25 - \log 0{,}05] = 8{,}72$$

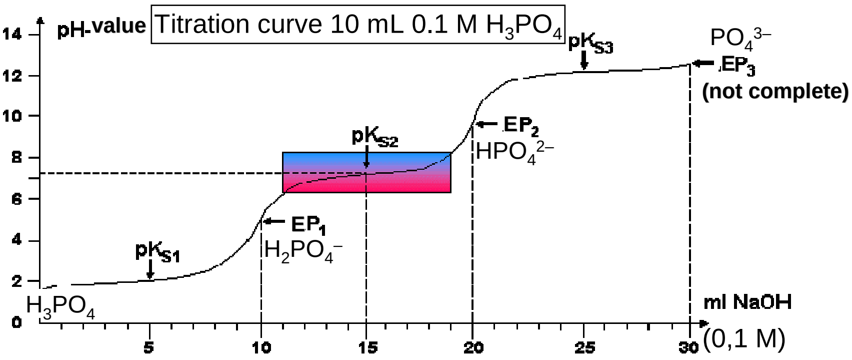
Titration Curve of Phosphoric Acid

Phosphoric acid dissociates in three steps:

$H_3PO_4 + H_2O \longrightarrow H_2PO_4^- + H_3O^+$ $pK_{S1} = 2{,}0$

$H_2PO_4^- + H_2O \longrightarrow HPO_4^{2-} + H_3O^+$ $pK_{S2} = 7{,}2$

$HPO_4^{2-} + H_2O \longrightarrow PO_4^{3-} + H_3O^+$ $pK_{S3} = 12{,}3$



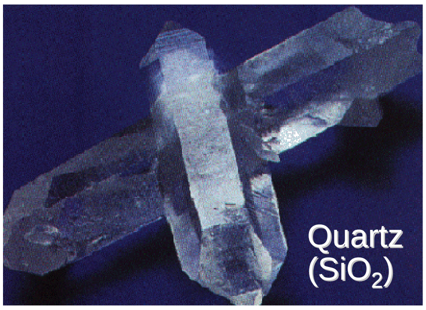
4.2 Salts, Solubility
The Crystalline State

Microscopic characteristics of the ***crystalline state*** is:
- 3D ***regular spatial arrangement (crystal lattice)***
- of ions (salts), atoms (metals), or molecules
- with high ***symmetry and long range order***.

Macroscopic crystals: flat surfaces, high symmetry.

Examples:


CaF_2

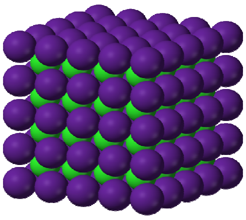

Quartz (SiO_2)

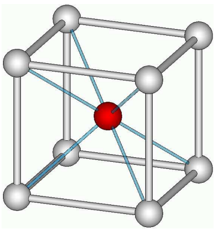
Such single crystals are transparent, but refractive.
Polycrystalline material (µm size crystals) are opaque.

Crystal Lattice

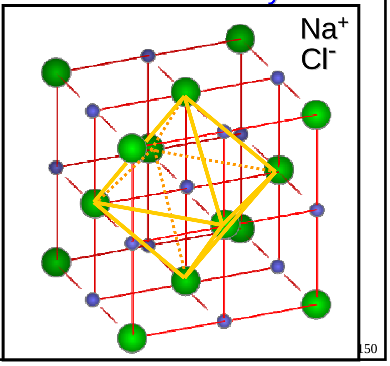
Different types of atomic crystal lattices exist, which are represented in the external shape of the macroscopic crystal: Cubic, tetragonal, hexagonal, monoclinic, triclinic. Dense sphere packing is sought ⇒ highest lattice energy; arrangement of counter ions electric neutral. Crystal type depends on ratio of ion radii r(cation):r((anion).

CsCl-type: Cs^+:Cl^- > 0,7 ⇒ cubic body-centered lattice; Each Cs^+ surrounded by 8 Cl^- (and vice-versa).





NaCl-type: Na^+:Cl^- <0,7 ⇒ cubic face-centered. Each Na^+ surrounded by 6 Cl^-



In ZnS-(Zincblende)-type: Zn^{2+}:S^{2-}<0,4 ⇒ coordination number 4.

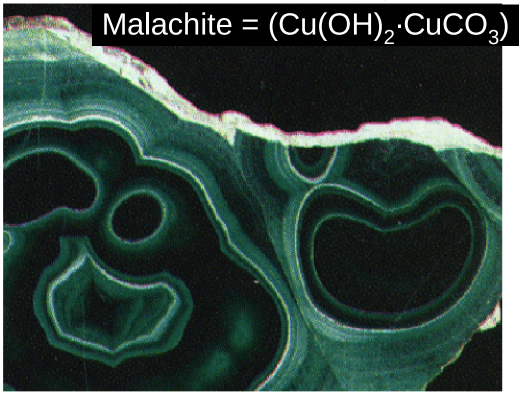
Amorphous State

The ***amorphous state*** is formed by the same molecular entities as the crystal lattice (ions, molecules), but ***without long range order***. Also denoted as ***glassy state***.

Amorphous solids have bent fracture surfaces.
Examples: Glasses and sediments like flint stone, opal and

Anisotropy is the property of being directionally dependent.
E. g. refractive index

Crystals are anisotropic;
Amorphous bodies
are isotropic.


Malachite = $(Cu(OH)_2 \cdot CuCO_3)$

Salts

Salts are ionic solids, in which the cations (+) and anions (-) are arranged regularly in a 3D ***crystal lattice***.
Due to the strong electrostatic attractions between oppositely charged ions (lattice energy) salts have high melting points (NaCl 800°C).

Salt crystals are electrically neutral, i. e. the charges of cations and anions are balanced = no net charge.

In salts of main group elements (I, II, VI, VII) the monoatomic ions comply with the octet rule ⇒ defined stoichiometry: (NaCl, $MgCl_2$, Na_2S)
Salts of auxiliary group elements (transition metals) often have variable valancy:

$FeCl_2 = \{Fe^{2+}2Cl^-\}$ = iron(II)-chloride
$FeCl_3 = \{Fe^{3+}3Cl^-\}$ = iron(III)-chloride
$Cu_2O = \{2Cu^+O^{2-}\}$ = copper(I)-oxide
$CuO = \{Cu^{2+}O^{2-}\}$ = copper(II)-oxide

Salts can also be composed of polyatomic ions:
Ammonium- NH_4^+, Carbonate- CO_3^{2-}, Sulfate- SO_4^{2-}, Phosphate- PO_4^{3-}
Dichromate- $Cr_2O_7^{2-}$, Permanganate- MnO_4^-.
Composition of the salt with according to charge balance; e. g.:
$KMnO_4=\{K^+MnO_4^-\}$, $K_2Cr_2O_7=\{2K^+Cr_2O_7^{2-}\}$; $(NH_4)_2CO_3=\{2NH_4^+CO_3^{2-}\}$

Salts and Minerals (Trivial names)

A **mineral** is a naturally occurring solid chemical substance formed through biogeochemical processes, having characteristic composition, highly ordered atomic structure, and specific physical properties


NaCl=table salt= rocksalt=halite

Common minerals:
Sandstone = sedimented quartz grains (SiO_2)
Chalk = calcium carbonate ($CaCO_3$)⇒
Lime stone = Calcium carbonate, too ($CaCO_3$), ⇒
Marble = Calcium carbonate, too ($CaCO_3$)
Gypsum = Calcium sulfate ($CaSO_4$)

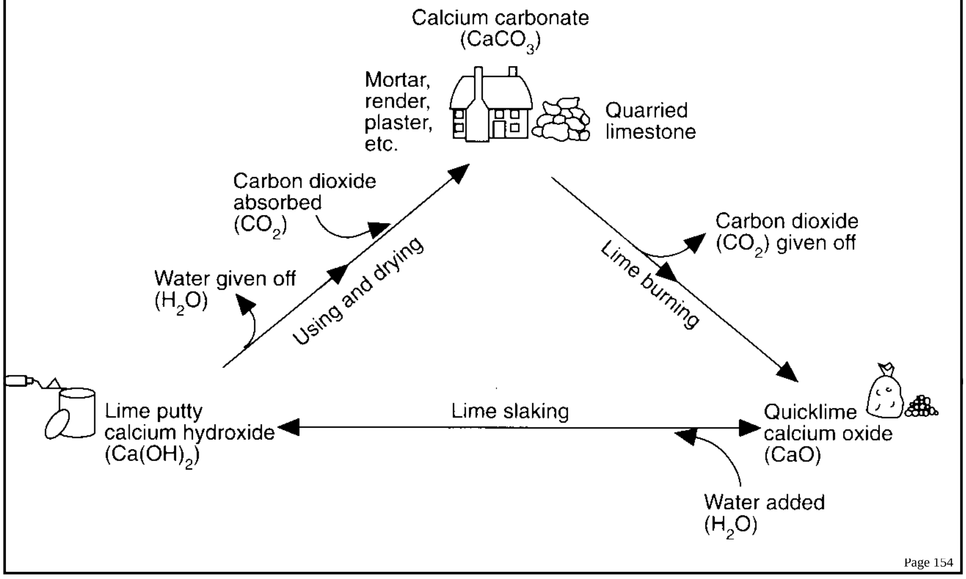
Sulfidic minerals:
Zincblende (ZnS),
Pyrite (FeS_2),
Galena (PbS)

Oxides: Corundum (Al_2O_3);
Iron oxides: Hematite (Fe_2O_3),
Magnetite (Fe_3O_4), Wüstite (FeO)

Silicates: Si-Oxides with Al, Fe, Mg, Na, K, ions.
Most rock-forming minerals

Other important minerals
Bauxite: mainly $Al(OH)_3$
Chile niter: $NaNO_3$

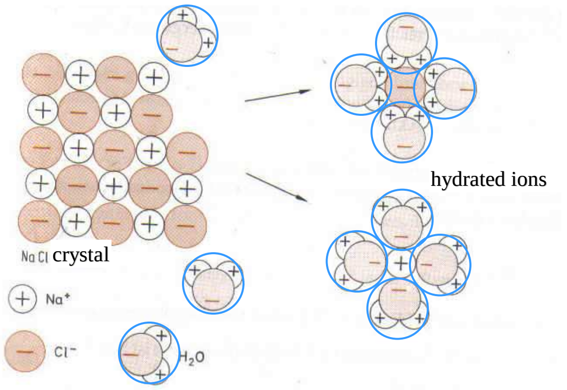
Lime Cycle



Solvation of Salts
Hydrate Shell

Ion crystals can be dissolved preferably in the polar solvent water. At surface water molecules are attracted by the ions; ions are dissolved. They are surrounded by a ***hydrate shell***. (hydration)

Solvation of NaCl in water:



Solubility Product

The solubility of a certain ionic compound in the respective solvent is limited. The solubility of salts quantified by the ***solubility product***. Heterogeneous equilibrium between saturated solution of the salt and solid, sedimented salt: $A^+B^-{}_{(s)} \Leftrightarrow A^+{}_{(aq)} + B^-{}_{(aq)}$

Solubility product: $K_{Sp} = c(A^+) \cdot c(B^-)$

Form of solubility product depends on stoichiometry:

<u>Example:</u> $A^{2+}2B^-{}_{(s)} \rightarrow A^{2+}{}_{(aq)} + 2B^-{}_{(aq)}$ e. g. $CaCl_2$

$KSp = c(A^{2+}) \cdot c^2(B^-)$ and for Al_2O_3 ?

If product of ion concentration < K_{Sp} ⇒ unsaturated solution;
If product of ion concentration > as K_{Sp} ions crystallize as salt.

The solubility product is temperature dependent.

(like all equilibrium constants)

Solubility Products
Poor Solubility Salts

Low solubility: $K_{Sp} < 10^{-4}\ mol^2/L^2$

Compound	K_{Sp}	Compound	K_{Sp}
Halogenides		**Sulfates**	
AgCl	$10^{-10}\ mol^2/l^2$	$CaSO_4$	$2 \cdot 10^{-5}\ mol^2/l^2$
AgBr	$5 \cdot 10^{-13}\ mol^2/l^2$	$BaSO_4$	$1 \cdot 10^{-9}\ mol^2/l^2$
AgI	$8 \cdot 10^{-17}\ mol^2/l^2$	$PbSO_4$	$1 \cdot 10^{-8}\ mol^2/l^2$
Carbonates		**Sulfides**	
$CaCO_3$	$5 \cdot 10^{-9}\ mol^2/l^2$	HgS	$10^{-54}\ mol^2/l^2$
$BaCO_3$	$2 \cdot 10^{-9}\ mol^2/l^2$	CuS	$10^{-36}\ mol^2/l^2$
Hydroxides		CdS	$10^{-28}\ mol^2/l^2$
$Mg(OH)_2$	$10^{-11}\ mol^3/l^3$	PbS	$10^{-28}\ mol^2/l^2$
$Al(OH)_3$	$10^{-33}\ mol^4/l^4$	ZnS	$10^{-22}\ mol^2/l^2$
$Fe(OH)_2$	$10^{-15}\ mol^3/l^3$	NiS	$10^{-21}\ mol^2/l^2$
$Fe(OH)_3$	$10^{-38}\ mol^4/l^4$	MnS	$10^{-15}\ mol^2/l^2$
$Cr(OH)_3$	$10^{-30}\ mol^4/l^4$	Ag_2S	$10^{-50}\ mol^3/l^3$

Hints:

- alkali metal salts have good solubility
- alkali earth salts have lower solubility
- Heavy metal salts (Ag, Pb, Ba, Cd) poorly soluble
- Sulfides (S^{2-}) are poorly soluble

Precipitation Reactions

Silver nitrate ($AgNO_3$) is the best soluble silver salt. What happens, if a sodium chloride solution is added to a saturated solution of silver nitrate?

$$Ag^+_{(aq)} + NO^-_{3(aq)} + Na^+_{(aq)} + Cl^-_{(aq)} \rightarrow ?$$

The solubility product of silver chloride (10^{-10}) is exceeded and the salt AgCl precipitates.

$$Ag^+_{(aq)} + NO^-_{3(aq)} + Na^+_{(aq)} + Cl^-_{(aq)} \rightarrow Na^+_{(aq)} + NO^-_{3(aq)} + \{Ag^+Cl^-\}\downarrow$$

The Solubility

Due to the different unit dimension K_{Sp} values are hard to compare.
Therefore, definition of the solubility S of a salt:

For $A^+B^-{}_{(s)} \rightarrow A^+{}_{(aq)} + B^-{}_{(aq)}$ $\qquad S = c(A^+) = c(B^-) = \sqrt{K_{Sp}}$

Example: $K_{Sp}\ (AgCL) = 10^{-10}\ mol^2/L^2$ $\quad L_{AgCl} = \sqrt{10^{-10}} = 10^{-5}\, mol/L$

$$c(Ag^+) = c(Cl^-) = c(AgCl) = 10^{-5}\, mol/L$$

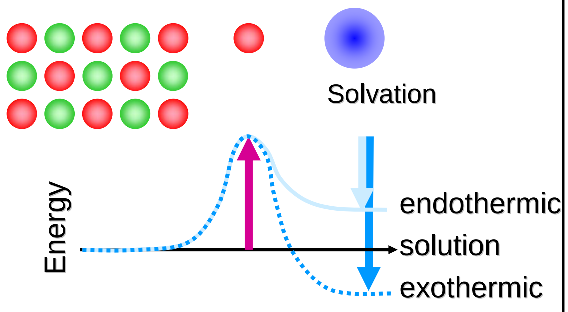
$$m = M \cdot n = 143{,}5 g/mol \cdot 10^{-5} mol = 1{,}435 mg$$

For the general case of a salt A_xB_y:

$$S = \frac{c(A^{y+})}{x} = \frac{c(B^{x-})}{y} = \sqrt[x+y]{\frac{K_{Sp}}{x^x \cdot y^y}}$$

Temperature Dependence of the Solubility

The dissociation of ions from the crystal is a highly endothermic (energy consuming) process .
In contrast, energy is released when the ion is solvated.



Lattice energy
\- Solvation energy
= Solution energy

Solution energy > 0 ⇒ endothermic process
Solution energy < 0 ⇒ exothermic process.

Most solution processes are endothermic
⇒ improved solubility at higher temperatures.

$$A^+B^-{}_{(s)} + Energie \overset{\leftarrow}{\longrightarrow} A^+{}_{(aq)} + B^-{}_{(aq)}$$

Common-Ion Effect

The common-ion effect is the decrease of the solubility of one salt, when another salt, which has an ion in common with it, is also present. For example, the solubility of silver chloride, AgCl, is lowered when sodium chloride, a source of the common ion chloride, is added.

Example: An amount of NaCl-solution is added to a saturated AgCl-solution, so that $c(Cl^-)=10^{-3}\ mol/L$. The solubility product of AgCl is exceeded; AgCl has to precipitate until: $K_{Sp} = c(Ag^+)\cdot c(Cl^-) = 10^{-10} mol/L$

The solubility product remains constant!

The concentration of silver ions $c(Ag^+) \neq c(Cl^-)$ is then:

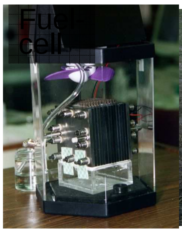
$$c(Ag^+) = \frac{K_{Sp}}{c(Cl^-)} = \frac{10^{-10}}{10^{-3}} = 10^{-7} mol/L$$

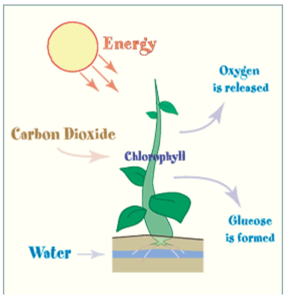
4.3 Redox Reactions Basics, Definitions

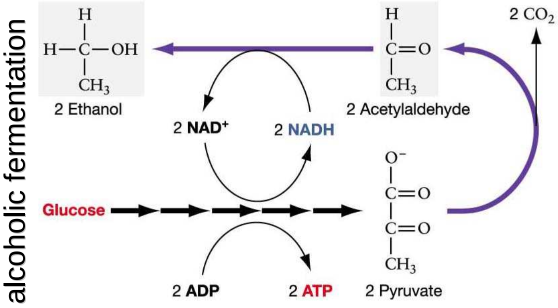
Redox reactions are essential for chemical energy storage and conversion:

Both in technology:

and in nature: Photosynthesis







Origin of the Terms Oxidation/Reduction

Originally the term o***xidation*** described the reaction of organic materials or metals with atmospheric oxygen; i. e. the combustion of wood, oil, wax or coal

$C + O_2 \rightarrow CO_2$

or the rust of iron

$4\ Fe + 3\ O_2 \rightarrow 2\ Fe_2O_3$

Reduction was the recovery of (precious) metals from their respective salts e. g.: $2\ HgO \rightarrow 2\ Hg + O_2$

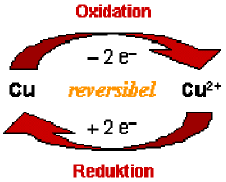
Since there are many similar processes, which don't involve oxygen, the term ***oxidation*** nowadays is used in a more general concept.

Today's Definition of Oxidation/Reduction

Oxidation is the loss of electrons by an atom, ion or molecule
⇒ increase of oxidation number (state)

Oxidation = Electron donation $A \rightarrow A^+ + e^-$

A transfer of electrons changes material properties substantially:
E.g.: Copper (red shiny metal) is transformed into Cu^{2+} ions.
Cu^{2+}-Ions form together with anions salts or are solvated.
Solvated Cu^{2+} ions have a hydrate sheath and blue color.



This process is reversible

Reduction is the gain of electrons by an atom, ion or molecule
⇒ decrease of oxidation number (state)

Reduction = Electron acceptance: $B + e^- \rightarrow B^-$

Redox Reaction
Thermite Reaction

Iron oxide powder mixed with aluminum powder.
Reaction initiated with sparkler or blowpipe (activation energy!).

Exothermic reaction!
Energy released as heat and light.

$Fe_2O_3 + 2\,Al \rightarrow Al_2O_3 + 2\,Fe$

How can you prove that the produced metal is iron, not aluminum?

Thermite process used for welding rails

Redox Reactions
Examples

No free electrons exist! ***Oxidation*** and ***reduction*** coexistent!

Redox reaction = Electron transfer: $A + B \rightarrow A^+ + B^-$

Depending on the reactants several electrons can be transferred

In redox reactions the gain of electrons in the reduction must be identical to the loss of electrons in the oxidation.
Electrons never show up in the total equation!

Example: Zinc + sulfur: Oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$
Reduction: $S + 2\,e^- \rightarrow S^{2-}$
Redox reaction: $\overline{Zn + S \rightarrow Zn^{2+} + S^{2-}} = ZnS$

A redox reaction can formally be subdivided into oxidation and reduction. The two parts reaction never occur separately!

Conservation of mass and charge: On both sides of reaction arror same number of the atoms of each element and same total charge.

Note: Do not subtract electrons $\cancel{Zn - 2e^- \rightarrow Zn^{2+}}$
No half molecules : $\cancel{\tfrac{1}{2}\,Cl_2}$

Balancing of Redox Equations

Aluminum reacted with bromine yielding aluminum bromide:

Interim eq.: $Al + Br_2 \rightarrow AlBr_3$
Bromine diatomic,
Aluminum ion 3 valent,
Bromide 1 valent

Oxidation ⇒ oxidation number increases! $\overset{0}{Al} \rightarrow \overset{+III}{Al}{}^{3+} + 3e^-$

Reduction ⇒ oxidation number decreases! $\overset{0}{Br}_2 + 2e^- \rightarrow 2\overset{-I}{Br}{}^-$

Lost = gained electrons: Ox (·2); Red (·3)

$$\begin{array}{c} 2Al \rightarrow 2Al^{3+} + 6e^- \\ 3Br_2 + 6e^- \rightarrow 6Br^- \\ \hline 2Al + 3Br_2 \rightarrow 2Al^{3+} + 6Br^- = 2AlBr_3 \end{array}$$

Total equation by addition of partial reaction equations; e^- eliminated!

More Redox Reactions

Reduction of iron-(II)-oxide to iron:

Redox : $2\,FeO + C \rightarrow CO_2 + 2\,Fe$
Oxidation : $C + 2\,O^{2-} \rightarrow CO_2 + 4\,e^-$
Reduction: $2\,Fe^{2+} + 4\,e^- \rightarrow 2\,Fe$

Redox reaction without oxygen:

Redox: $2\,Na + Cl_2 \rightarrow 2\,NaCl$
Oxidation: $2\cdot(Na \rightarrow Na^+ + e^-)$
Reduction: $Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$

Na (I. mg) looses 1 e^-,
Cl (VII. mg) gains 1 e^-,
to obey octet rule.
Chlorine diatomic gas.

Redox reaction with complex stoichiometry:

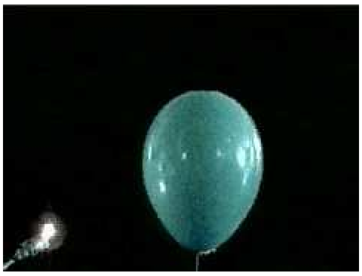
Redox: $16\,Al + 3\,S_8 \rightarrow 8\,Al_2S_3 = \{2Al^{3+}3S^{2-}\}$
Oxidation: $16\cdot(Al \rightarrow Al^{3+} + 3\,e^-)$
Reduction: $3\cdot(S_8 + 16\,e^- \rightarrow 8S^{2-})$

Al (III. mg) looses 3 e^-,
S (VI. mg) gains 2 e^-,
to obey octet rule.
sulfur as S_8 ring.

The stoichiometric factors result from combination of the partial reaction steps.

Oxyhydrogen Reaction

Many redox reaction are exothermic, i. e. release of energy.
Another reaction this kind the oxyhydrogen reaction (hydrogen test)



$2\ H_2 + O_2 \rightarrow 2\ H_2O$ + energy

Biggest hydrogen-oxygen reaction of all times?

Zeppelin "Hindenburg"
Lakehurst 1937

Oxidation: $H_2 \rightarrow 2\ H^+ + 2\ e^-$
Reduction: $O_2 + 4\ e^- \rightarrow 2\ O^{2-}$
Redox: $2\ H_2 + O_2 \rightarrow (4H^+ + 2O^{2-}) \rightarrow 2H_2O$

H (I. mg) losses 1 e^-,
O (VI. mg) gains 2 e^-,
⇒ noble gas configuration.
Both diatomic gases!

Oxidizer/Reducer

Compounds which are able to oxidize other species (eliminate electrons) are called oxidizers (oxidants, oxidizing agents) = electron acceptors
The oxidizer itself is being reduced!

Common oxidizers:

- Oxygen $O_2 + 4\ e^- \rightarrow 2\ O^{2-}$
- Chlorine $Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$
- Oxoanions z.B.: MnO_4^- (Permanganate), $Cr_2O_7^{2-}$ (Dichromate)
- Anions of halogen oxoacids, z.B. ClO_4^- (Perchlorate)
- Noble metal ions, e. g. $Ag^+ + e^- \rightarrow Ag$

Compounds which are able to reduce other species (donate electrons) are called reducers (reductants, reducing agents) = electron donators
The reducer itself is being oxidized!

Common reducers:

- Hydrogen $H_2 \rightarrow 2\ H^+ + 2\ e^-$
- Zn, Fe, Mg $Zn \rightarrow Zn^{2+} + 2e^-$
- Carbon

Oxidation Numbers/State

How do you know, its a redox reaction
and which species gains or looses how many electrons?

Redox reaction ⇒ change of oxidation numbers

Oxidation number = **hypothetical** charge an atom would have if all bonds to atoms of different elements were 100% ionic.

Rules (order of priority) agreed-upon for determ. of oxidation state (roman numeral superscript):

1. Free elements always have oxidation number 0
2. Monoatomic ions: OxNo = charge
3. H OxNo = +I ; O OxNo = -II
   (exception: Hydrides $Me\overset{-I}{H}_x$; $\overset{+I}{H}_2\overset{-I}{O}_2$)
4. In molecules ΣOxNo=0 ;
   in molecular ions ΣOxNo= charge

Examples:

$\overset{0}{H_2}, \overset{0}{Cl_2}, \overset{0}{Na}, \overset{0}{Al}$

$\overset{+I}{Na^+}, \overset{+II}{Ca^{2+}}, \overset{-II}{S^{2-}}$

$\overset{-IV}{C}\overset{+I}{H}_4, \overset{+IV}{C}\overset{-II}{O}_2$

$\overset{+VII}{Mn}\overset{-II}{O}_4^-, \overset{+VI}{S}\overset{-II}{O}_4^{2-}$

Oxidation Numbers of Selected Compounds

Compounds of chlorine with various oxidation numbers:

OxNo	-I	0	+I	+IV	+V	+VII
Formula	Cl^-	Cl_2	ClO^- $HClO$	ClO_2	ClO_3^- $HClO_3$	ClO_4^- $HClO_4$
Name	Chloride	Chlorine	Hypochlorite hypochloric acid	Chloro-dioxide	Chlorate Chloric acid	Perchlorate Perchloric acid

Compounds of sulfur with various oxidation numbers:

OxNo	-II	0	+III	+IV	+VI
Formula	S^{2-}/H_2S	S_8	$S_2O_4^{2-}$	$SO_2/SO_3^{2-}/H_2SO_3$	$SO_3/SO_4^{2-}/H_2SO_4$
Name	Sulfide/Hydrogen sulfide	Sulfur	Dithionite	Sulfur dioxide sulfurous ac.	S.trioxide/Sulfate sulfuric acid

Compounds and oxidation numbers of manganese:

OxNo	+II	+IV	+VI	+VII
Formula	Mn^{2+}	MnO_2	MnO_4^{2-}	MnO_4^-
Name	Manganese (II) ion	Manganese dioxide	Manganate (blue)	Permanganate (violet)

Redox Reactions and pH-Value

In some redox reactions (often in aqueous solution)
H_3O^+ resp. OH^- ions for the charge compensation
under consideration of the acidic or alkaline/basic environment

E.g.: Permanganate reduced to manganese(II) in acidic environment

$$\overset{+VII}{MnO_4^-} + 5\,e^- \rightarrow \overset{+II}{Mn^{2+}}$$

For compensation fo charges (left -6; right +2) 8 H_3O^+ are introduced (acidic environment).

$$MnO_4^- + 5\,e^- + 8\,H_3O^+ \rightarrow Mn^{2+} + 12\,H_2O$$

Together with 4 O^{2-} (formally) they form 12 H_2O

E.g.: Hydrogen peroxide is oxidized to oxygen in alkaline.

$$\overset{-I}{H_2O_2} \rightarrow \overset{0}{O_2} + 2\,e^- + 2\,H^+$$

Note: There are no free protons!

$$H_2O_2 + 2\,OH^- \rightarrow O_2 + 2\,e^- + 2\,H_2O$$

Both examples only **partial** reaction equations!

Redox Titration
Example: Permanganometry

Redox reactions can be used in quantitative analysis (titration) for determination of an unknown concentration of a solution,
if the equivalence point is detectable, e. g. change of color
Permanganometry: Titration of a solution of an oxidizable compound (e. g. Fe^{2+}) with potassium permanganate solution ($KMnO_4$; violet);
The Fe^{2+} are oxidized by the drop wise added MnO_4^- ions gradually yielding Fe^{3+} ions. At the same time the violet MnO_4^- ions are reduced to colorless Mn^{2+} ions ⇒ decolorization of the added permanganate solution as long as Fe^{2+} ions are present.
After equivalency (Fe^{2+} ions consumed) no reaction of added MnO_4^- ions⇒ violet coloring of the iron ion solution.

$$\begin{array}{lccc}
Ox.: & Fe^{2+} & \rightarrow & Fe^{3+} + e^- \\
Red.: & \boxed{MnO_4^-} + 8H_3O^+ + 5e^- & \rightarrow & Mn^{2+} + 12H_2O \\
Redox: & \boxed{MnO_4^-} + 8H_3O^+ + 5Fe^{2+} & \rightarrow & Mn^{2+} + 12H_2O + 5Fe^{3+}
\end{array}$$

From volume and concentration of consumed permanganate solution the concentration of Fe^{2+} solution can be calculated.
Account for stoichiometry! 1 mol MnO_4^- oxidizes 5 mol Fe^{2+}.

Chromatometry, Iodometry

Two other analytic methods like permanganometry (titrations) but with different stoichiometry:

Chromatometry (dichromate titration):

$Cr_2O_7^{2-} + 6\ Fe^{2+} + 14\ H_3O^+ \rightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 21\ H_2O$

Dichromate

Iodometry: determination of concentration by means of redox system $2\ I^- \Rightarrow I_2 + 2\ e^-$: Elemental iodine forms with starch solution a deep blue complex.

Reversed titration method:

Example: determination c(Cu^{2+}):

- Measure off defined volume (e. g. 20 ml)
- Add excess of KI solution ⇒ $2\ Cu^{2+} + 2I^- \rightarrow 2\ Cu^+ + I_2$
- 2 mol Cu^{2+} produce 1 mol I_2, which dyes the solution blue
- Determination of the molar of produced iodine by redox titration with reductant solution of known concentration.
- $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ (2 mol thiosulfate reduces 1 mol iodine)
- From vol. and conc. of used $S_2O_3^{2-} \Rightarrow n(I_2) \Rightarrow n(Cu^{2+}) \Rightarrow c(Cu^{2+})$

Noble/Base Metals

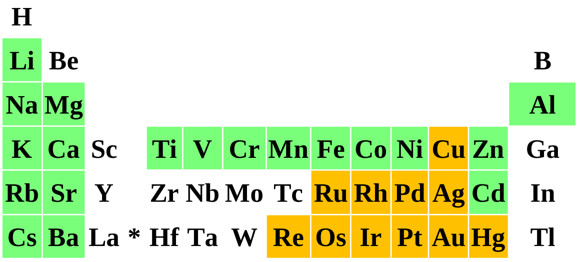
Why does iron rust, but gold does not? Does aluminum oxidize? What is the difference between noble and base metals?

In general all metals can react by loosing electrons, forming metal kations, i. e. they oxidize. But:

The various metals have a different oxidizability:

Noble metals: resistant to oxidation, low reactivity, occur in elemental form. Gold, platinum, silver, (copper)

Base metals: readily oxidizable, reactive, occur in compounds all main-group metals: (Alkali, alkaline earth metals, aluminum) Transition metals: Iron, Zinc, etc.

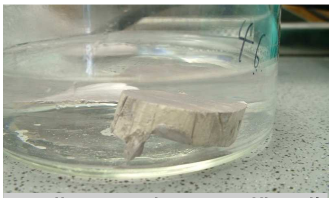


H													
Li	Be												B
Na	Mg												Al
K	Ca	Sc		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
Rb	Sr	Y		Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
Cs	Ba	La	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl

Chemical Reactivity (Oxidizability) of Alkali Metals

Alkali metals have highest reactivity. Storage in inert media (ether) or paraffin oil. Otherwise intense reactions, like

$4\ Na + O_2 \rightarrow 2\ Na_2O$



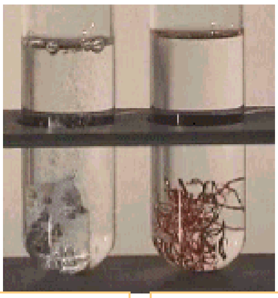
Sodium under paraffin oil

Water not feasible as storage medium, since sodium (like all alkali metals) reacts with water.

Sodium hydroxide is produced and hydrogen, which is inflamed. The sodium melts (T_m=98°C) due to reaction heat

---

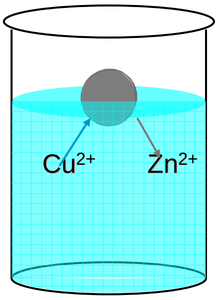
Redox Reactions of Noble and Base Metals



$Zn + 2\ HCl \rightarrow Zn^{2+} + 2Cl^- + H_2\uparrow$

$Cu + 2HCl \not\rightarrow$

Why?



$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Table of Noble/Base Metals

noble ↑

- Gold
- Platinum
- Palladium
- Mercury
- Silver
- Copper
- Lead
- Tin
- Nickel
- Cobalt
- Cadmium
- Iron
- Chromium
- Zinc
- Aluminum
- Magnesium
- Sodium
- Calcium
- Potassium
- Lithium

reactive ↓

↑ decreasing oxidizability

↓ increasing reducing reaction

The oxidizability of metals, i. e. their tendency to loose electrons, can be compared by direct reaction with each other ⇒ ranking

Examples:

$Ag + Au^{+} \rightarrow Ag^{+} + Au$

$Cu + 2\,Ag^{+} \rightarrow Cu^{2+} + 2\,Ag$

$Ni + Cu^{2+} \rightarrow Ni^{2+} + Cu$

$Fe + Ni^{2+} \rightarrow Fe^{2+} + Ni$

$Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

but: $Cu + Zn^{2+} \rightarrow$

Driving force for the oxidation of base metals by noble metal kations is: $\Delta G < O$

How can the tendency of electron attraction or repulsion be quantified?

How can the energy released in redox reactions be utilized?

Conversion of Energy

Chemical energy $\longrightarrow$ Heat z.B.: $C + O_2 \rightarrow CO_2$

Oder: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Electric energy $\underset{\text{Dynamo}}{\overset{\text{Electric motor}}{\rightleftarrows}}$ Mechanical energy

Chemical energy $\xrightarrow{\text{Battery}}$ Electrical energy

Spatial separation of oxidation ($Zn \rightarrow Zn^{2+} + 2e^{-}$) and reduction ($Cu^{2+} + 2e^{-} \rightarrow Cu$) reaction. Instead of direct transfer from oxidation to reduction site. electrons have to flow through conductor.

Chemical energy $\overset{\text{Accumulator}}{\leftrightarrows}$ Electrical energy

4.4 Electrochemistry: Redox Potential; Galvanic (Voltaic) Cell

Between a metal bar (electrode) and the surrounding metal ion solution (electrolyte) charges are exchanged by chemical reactions building up a difference in the chemical potential. More noble metals have a lower tendency to loose electrons. If two such half-cell are connected by a conductor ***the potential difference*** ΔE can be measure as voltage.

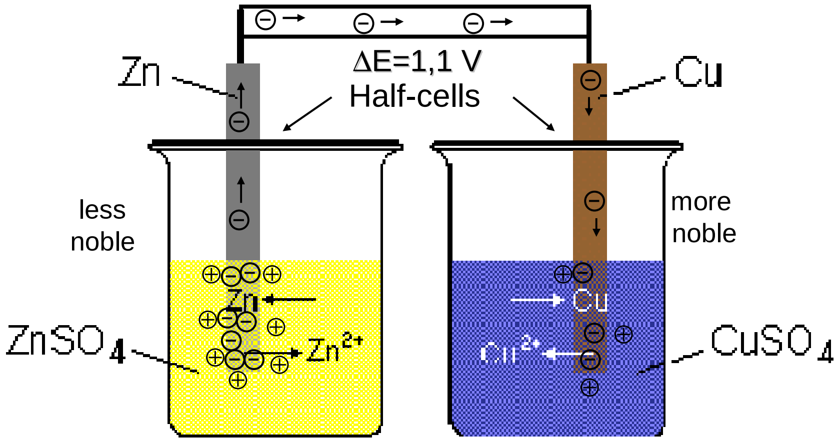


Table of Standard Electrode Potenials

Strength oxidizing/reducing agents depends on change of Gibbs free energy ΔG during electron loss or gain: Each ***redox system (electrode/ electrolyte*** ⇒ ***redox potential***; listed in Table of Standard Electrode Potential.

Isolated potential (half-cell)= not obtained emp. ⇒ only galvanic cell potial between pairs of electrodes ΔE. E_0 ***Hydrogen Electrode*** defined 0

Stronger oxidizers (Ox)

⇒ positive ***potential ΔE_0***

Stronger reduction agents (Red)

⇒ negative ***potential ΔE_0***

Stand.cond.(25°C,1013 hPa,1 mol/L).

$$\Delta_R G_0 = -n_e \cdot F \cdot \Delta E_0 \qquad \text{Faraday-Konst. F}$$

Base metals oxidized by acid ($H^+ \Rightarrow H_2$ noble metals and copper are not.

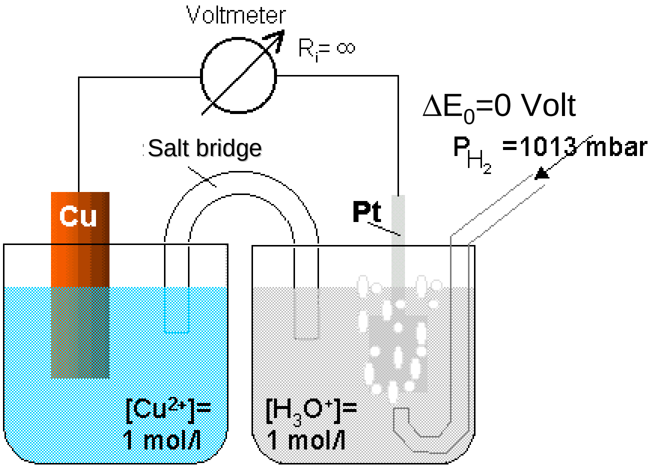
increasing oxidation activity

	Ox.	n_e	Red.	ΔE_0
Fluor (F)	F_2	+ 2e$^-$	↔ 2F$^-$	+2,87 V
Gold (Au)	Au^+	+ e$^-$	↔ Au	+1,69 V
Platinum (Pt)	Pt^{2+}	+ 2e$^-$	↔ Pt	+1,20 V
Chlorine (Cl)	Cl_2	+ 2e$^-$	↔ 2Cl$^-$	+1,31 V
oxygen (O_2)	O_2+4H$^+$	+ 4e$^-$	↔2 H_2O	+0,85 V
Silver (Ag)	Ag+	+ e$^-$	↔ Ag	+0,80 V
Sulfur (S)	S	+ 2e$^-$	↔ S^{2-}	+0,48 V
Copper (Cu)	Cu^{2+}	+ 2e$^-$	↔ Cu	+0,35 V
hydrogen (H_2)	**2H$^+$**	**+ 2e$^-$**	**↔ H_2**	**0**
Lead (Pb)	Pb^{2+}	+ 2e$^-$	↔ Pb	-0,13 V
Tin (Sn)	Sn^{2+}	+ 2e$^-$	↔ Sn	-0,14 V
Nickel (Ni)	Ni^{2+}	+ 2e$^-$	↔ Ni	-0,23 V
Cadmium (Cd)	Cd^{2+}	+ 2e$^-$	↔ Cd	-0,40 V
Iron (Fe)	Fe^{2+}	+ 2e$^-$	↔ Fe	-0,41 V
Zinc (Zn)	Zn^{2+}	+ 2e$^-$	↔ Zn	-0,76 V
Aluminum (Al)	Al^{3+}	+ 3e$^-$	↔ Al	-1,66 V
Magnesium (Mg)	Mg^{2+}	+ 2e$^-$	↔ Mg	-1,66 V
Sodium (Al)	Na^+	+ 1e$^-$	↔ Na	-2,71 V
Lithium (Li)	Li^+	+ 1e$^-$	↔ Li	-3,02 V

increasing reducing activity

Standard Hydrogen Electrode (SHE)

Determination of standard electrode potentials in comparison to Standard Hydrogen Electrode (set to ΔE_0=0 V)

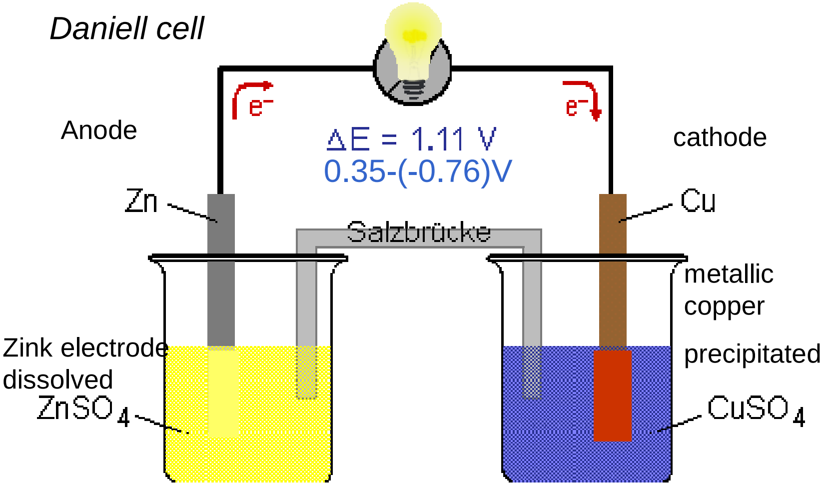


Galvanic Cell / Voltaic Element
Electromotive Force (EMF)

Combination of two halb-cells is a Galvanic Cell

ΔE_0= ΔE_0 (cathode) -ΔE_0 (Anode) = EMF (Electromotive Force)

Daniell cell



Nernst Equation

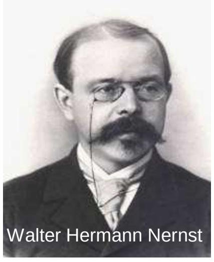
Concentration Dependence of Electrode Potential

The potential of a real electrode depends on the standard potential of the redox system (electrode/electrolyte) an on the conditions (concentration, pressure, temperature).
Under standard condition (c = 1mol/L solution,1013 hPa, 25°C)
the ***standard*** potential E^0 is listed in the table.

For higher or lower concentration of the electrolyte the electrode potential of the half-cell E can be calculated by the Nernst equation:

$$\boxed{E = E^0 + \frac{0{,}059}{n} \cdot \log c(Me^{n+})}$$

Nernst
equation


Walter Hermann Nernst

Example: What is the potential of a copper electrode in a Cu^{2+}-ion solution of c = 0,1 mol/L?

$$E = 0{,}35 + \frac{0{,}059}{2} \cdot \log 10^{-1} = 0{,}35 + \frac{0{,}059}{2} \cdot (-1) = 0{,}3205V$$

Corrosion, Passivation

Corrosion: Disintegration of an engineered material
due to chemical reaction with its surrounding (oxygen, acid)

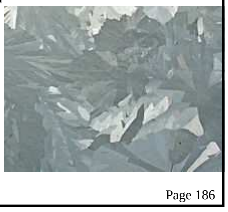
$$2Me + O_2 + 2H_2O \rightarrow 2Me^{2+} + 4OH^-$$

$$2Me + 2H_3O^+ \rightarrow 2Me^{2+} + 2H_2O + H_2 \uparrow$$

Basic metals oxidized by atmospheric oxygen ⇒ few nm oxide layer. Formation of hard, non-reactive surface film inhibits further corrosion (e.g. Al_2O_3 on Al, ZnO on Zn, TiO_2 on Ti),⇒ ***Passivation***)

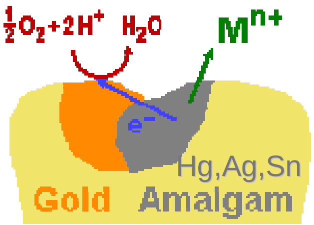
Iron, however, forms a porous oxide layer (rust). oxygen can penetrate rust layer until complete corrosion (Fe_2O_3, Fe_3O_4) (Pitting).

In hot-dip galvanizing process iron or steel are coated with a zinc layer by passing metal through molten zinc bath (460°C). Exposed to atmosphere, zinc reacts with O_2 to form ZnO and further with CO_2 to $ZnCO_3$, a dull grey, fairly strong material protecting the iron below against further corrosion (passivation). If the coating is damaged, zinc works as a galvanic anode so that iron is not oxidized.



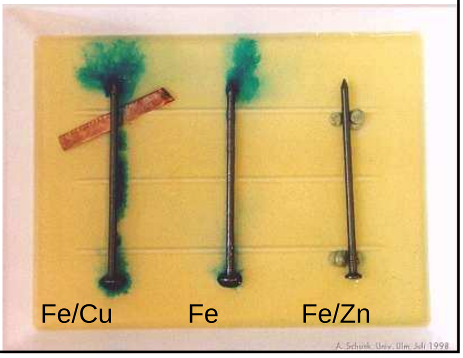
Galvanic Corrosion
Galvanic (Sacrificial) Anode

Galvanic Corrosion:
Short-circuited galvanic element;
Direct connection with a more noble metal enhances oxidation (corrosion) of the more basic metal, since electrons are deflected. Contact between gold and amalgam fillings should be avoided, otherwise mercury and tin are dissolved.



Galvanic anode: Basic metal (Zn, Mg, Al, alloy) in direct contact protects metal (Fe) from corrosion; itself being dissolved (sacrificed)
In ships, pipes, etc.

Iron nail in saline with indicator (with Fe^{3+} green dye):
Galvanic corrosion (contact with nobler Cu) enhances iron dissolution,
Galvanic anode from Zn stops corrosion. $Zn^{2+}(aq)$ colorless



Batteries:
Zinc-Carbon Battery (Dry Cell)

Anode (Minus pole, Zinc case):
$Zn \rightarrow Zn^{2+} + 2e^-$

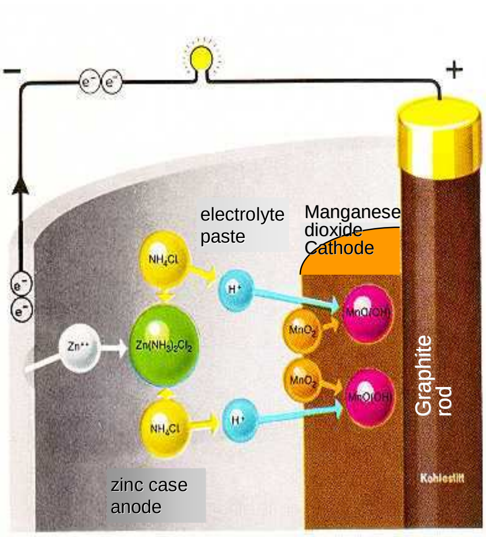
Cathode (Plus pole, carbon rod):
$\overset{+IV}{MnO_2} + H^+ + 1e^- \rightarrow \overset{+III}{MnO(OH)}$

Manganese dioxide → Manganoxid-hydroxid

Regeneration of H^+ from the Ammonium chloride electrolyte:
$NH_4^+ \rightarrow NH_3 + H^+$

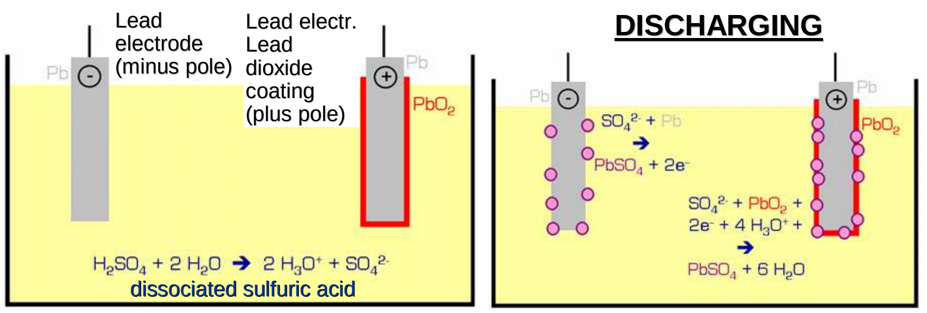
Zinc ions bind produced ammonia as complex:
$Zn^{2+} + 2NH_3 \rightarrow [Zn(NH_3)_2]^{2+}$

This complex forms with the chloride ions (ammonium chloride) a salt
$[Zn(NH_3)_2]^{2+} + 2Cl^- \rightarrow [Zn(NH_3)_2]Cl_2(s)$



Total reaction:
$Zn + 2MnO_2 + 2NH_4Cl \rightarrow 2MnO(OH) + [Zn(NH_3)_2]Cl_2$ all solid!

Lead-Acid Battery



$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$$
$$PbO_2 + SO_4^{2-} + 4H_3O^+ + 2e^- \longrightarrow PbSO_4 + 6H_2O$$

$$\overset{0}{Pb} + \overset{+IV}{PbO_2} + 2H_2SO_4 \overset{\text{discharge}}{\underset{\text{charging}}{\rightleftarrows}} \overset{+II}{2PbSO_4} + 2H_2O + elektrischeEnergie$$

discharge = comproportionation

charging = disproportionation

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^- | -0,36V$$
$$PbSO_4 + 6H_2O \longrightarrow PbO_2 + SO_4^{2-} + 4H_3O^+ + 2e^- | +1,68V$$
$$E^0_{Ges} = 1,68V - (-0,36V) = \underline{2,04V}$$

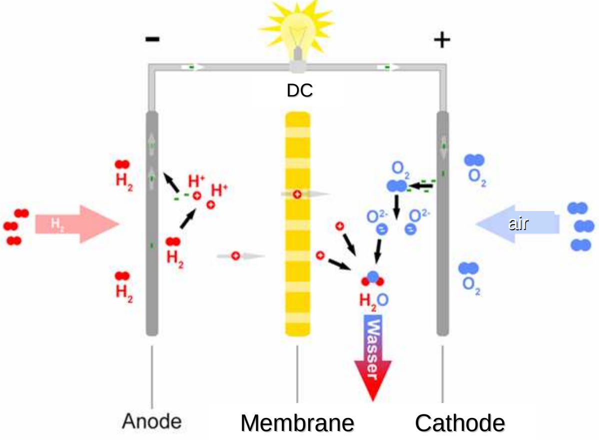
For car: 12 Volt stacking!

Fuel Cell

Idea: 1838 Christian Schönbein; since 1950 in space technology.

Electrodes separated by membrane or electrolyte. Anode flushed with fuel (H_2, methane, ethanol, glucose solution), cathode with oxidizing agent (O_2, H_2O_2). Electrodes made of carbon nano tubes with Pt- or Pd-coating as catalyst.

Theor. max.1,23 V: pract. 0,5-1 V ⇒ Stacking



<u>Typs:</u>

Alkaline Fuel Cell

H_2/ O_2/OH^- (100kW)

Direct Methanol Fuel Cell

MeOH/Luft/Polymer/H^+ (500 kW)

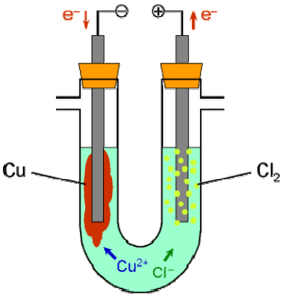
Electrolysis

Processes in voltaic cells can be reversible: Applying DC-voltage at electrodes leads to ***electrolysis***: Elements in the electolyte are separated by enforced redox reaction.

Voltaic cell
spontaneous

$Zn + Cu^{2+} \rightleftarrows Zn^{2+} + Cu$

Electrolysis
non-spontaneous



Electrolysis of copper chloride solution

Ion migration due to electrostatic attraction:
Positive Cations (Cu^{2+})→minus pole (cathode)
Negative Anions (Cl^-) → plus pole (anode)

Cathode: $Cu^{2+} + 2\ e^- \rightarrow Cu$ *Reduction*

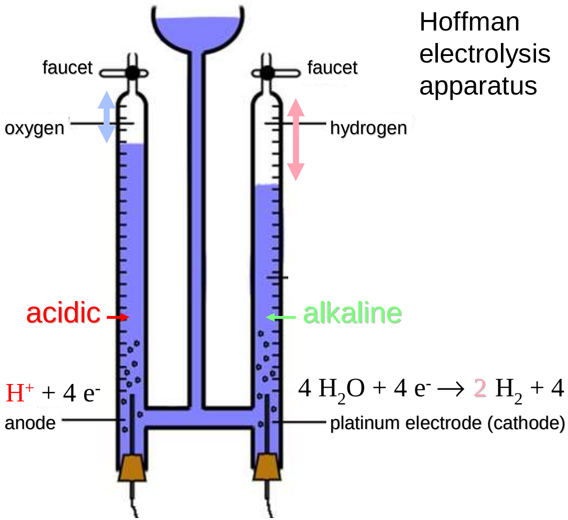
Anode: $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$ *Oxidation*

Note: Polarity of cathode/anode reversed with respect to voltaic element: Plus ⇄ minus pole

Oxidation ***always*** at the anode!

Electrolysis of Water

Hoffman
electrolysis
apparatus



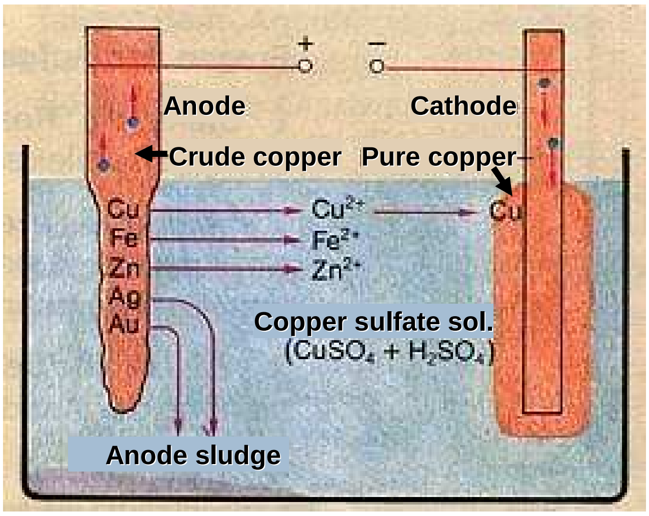
$2\ H_2O \rightarrow 1 O_2 + 4\ H^+ + 4\ e^-$

$4\ H_2O + 4\ e^- \rightarrow 2\ H_2 + 4\ OH^-$

15 Volt DC !

Electrolytic Copper Purification

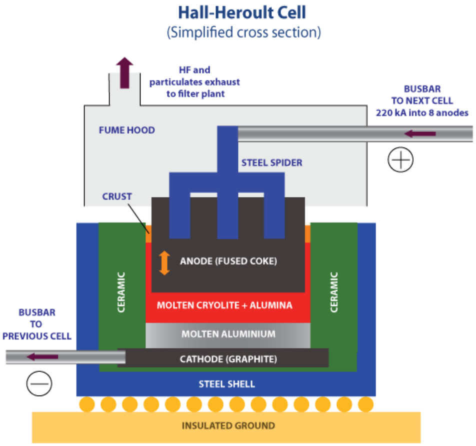
Crude copper anode (99,5% pure) dissolved at 0.2-0.3 V at anode. Highly pure copper (99,95%) precipitated at cathode. Impurities of base metals (Fe, Zn) remain in solution (as ions); noble metal particles are deposited on the ground (anode sludge).



Aluminum Production
Hall-Heroult Process

Aluminum ore (bauxite) heated in conc. NaOH sol. 200°C (Bayer proc.).
Aluminum hydroxide ⇒ sol. Aluminate
$Al(OH)_3 + NaOH \rightarrow Na^+ + [Al(OH)_4]^-$
Filtering of solid impurities;
Neutralisation → pure $Al(OH)_3$ precip.;
Calcination (1000°C) ⇒ Alumina.
$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$

Alumina dissolved in molten cryolite (Na_3AlF_6) at 1000°C in a ceramic vat; electro-chem. reduction to Aluminum 5 Volt DC, some 100,000 A current! Anodes of fused coke are consumed by oxidation:



$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$;
$\Delta H = +\ 0{,}835$ MegaJ/mol Al
Extreme energy consumption!