

# General Chemistry - Inorganic Chemistry

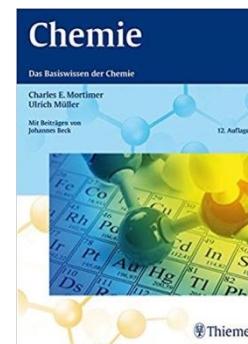
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# References

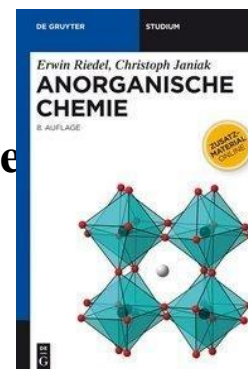
## Basics

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- **M. Binnewies, M. Jäckel, H. Willner, G. Rayner-Canham, Allgemeine und Anorganische Chemie, Spektrum, 1. Auflage 2004**
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## Advanced

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- **A.F. Hollemann, N. Wiberg, Lehrbuch der anorganischen Chemie deGruyter, 102. Auflage 2007**
- **J.E. Huheey, E.A. Keiter, R. Keiter, Anorganische Chemie deGruyter, 3. Auflage 2003**



# 1. Introduction

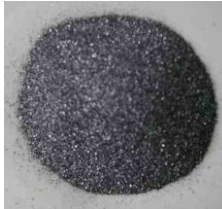
## What is Chemistry?

“Chemistry is the science of substances, their structure, their properties, and their conversion, which results in the formation of other substances“  
(Linus Carl Pauling 1956, Nobel prizes: Chemistry 1954, Peace 1962)

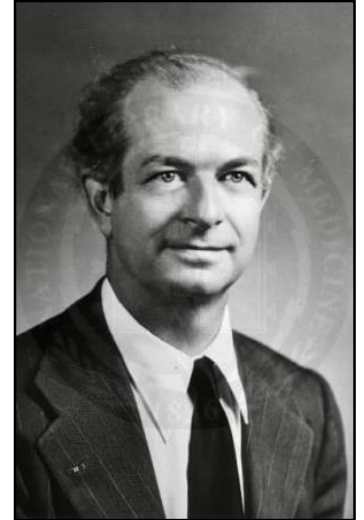
### Example



*Native quartz crystals*



Physical process (e.g. recrystallization and laser cutting)



# 1. Introduction

**Chemistry has been exponentially growing for the last 200 years**

**Number of original publications traceable in Chemical Abstracts (CA) up to 2016  
~ 42 mill. abstracts**

**Development of the number of publications per year**

<b>1830</b>	<b>400</b>
<b>1930</b>	<b>55000</b>
<b>1985</b>	<b>460000</b>
<b>1995</b>	<b>700000</b>
<b>2001</b>	<b>755000</b>

**More than 100 Mill. compounds and bio-sequences in CA database are registered today (2017):**

<b>Bio sequences</b>	<b>41%</b>
<b>Polymers</b>	<b>3%</b>
<b>Alloys</b>	<b>2%</b>
<b>Organics</b>	<b>47%</b>
<b>Inorganic</b>	<b>2%</b>
<b>Coordination compounds</b>	<b>5%</b>

**Historical development of the CA database**

<b>1957</b>	<b>Start of database</b>
<b>1990</b>	<b>10 Mill. compounds</b>
<b>2008</b>	<b>40 Mill. compounds</b>
<b>2009</b>	<b>50 Mill. compounds</b>
<b>2012</b>	<b>70 Mill. compounds</b>
<b>2015</b>	<b>100 Mill. compounds</b>
<b>2024</b>	<b>193 Mill. compounds</b>

## 2. Substances and Separation

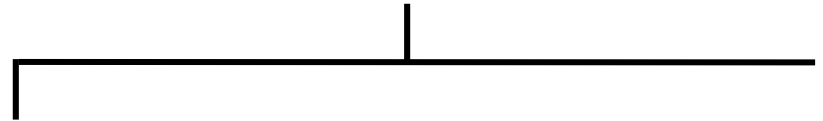
**Substances are Compounds, which chemical and physical Properties are independent of Size and Shape**

**Example: Stainless steel → driller, knife, frames, scissors, screws...**



Cold strip coils (Steel center ThyssenKrupp Steel Europe)

### *Substance*



#### *Heterogeneous substance*

*(non-uniform on a microscopic level)*

- Solid-Solid**      Solids mixtures (granite)
- Solid-Liquid**      Suspension (milk of lime)
- Solid-Gaseous**      Aerosol (smoke)
- Liquid-Liquid**      Emulsion (milk)
- Liquid-Gaseous**      Aerosol (fog, foam)

#### *Homogeneous substance*

*(uniform on a microscopic level)*

- Alloys (brass)**
- Solutions (NaCl-solution)**
- (Nanoscopic) Aerosols**
- Liquid solutions (ethanol in water)**
- Gas solutions (oxygen in water)**
- Pure substances**

# 2. Substances and Separation

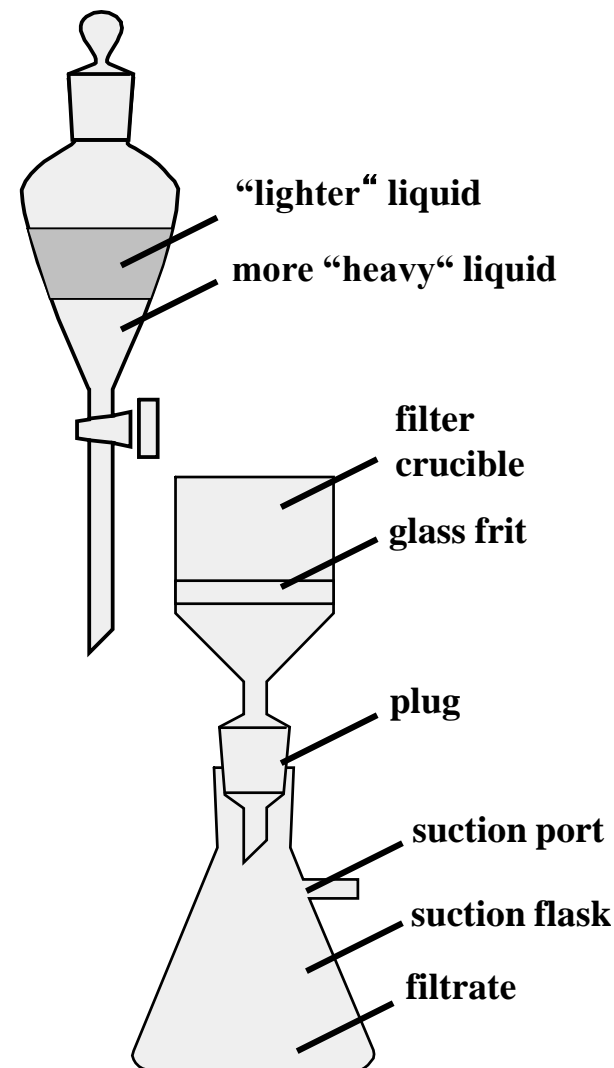
## Physical Methods for Separation of Heterogeneous Substances

### 1. Differences in density

<b>Solid-Solid</b>	<b>Re-slurry (washing of gold)</b>
<b>Solid-Liquid</b>	<b>sedimentation (1 G) centrifugation (up to <math>10^4</math> G)</b>
<b>Liquid-Liquid</b>	<b>separation (separating funnel)</b>

### 2. Differences in particle size

<b>Solid-Solid</b>	<b>sieve</b>
<b>Solid-Liquid</b>	<b>filtration (filter crucible)</b>
<b>Solid-Gaseous</b>	<b>filtration (air filter)</b>



# 2. Substances and Separation

## Separation of Homogeneous Systems

### 1. Physical methods

Vaporising and condensation:

Cooling:

Condensation and vaporising:

Adsorption and desorption

Gas chromatography

Liquid chromatography

Paper chromatography

Centrifugation (gases)

seawater → rainwater

salt solutions → salt crystals

air → N<sub>2</sub>, O<sub>2</sub>, noble gases

dissolution of vaporisable substances

dissolution of solid substances

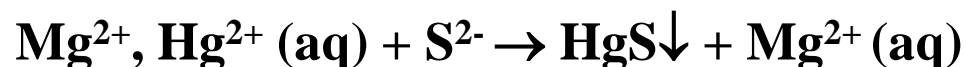
dissolution of solid substances (*β-carotene*)



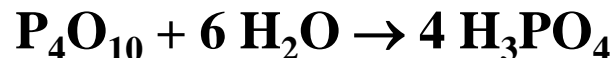
### 2. Chemical methods

Precipitation

Gas purification



drying of noble gases or N<sub>2</sub> via:



# 2. Substances and Separation

## Classification of Substances

**Heterogeneous substances**

system consists of different phases

**Homogeneous substances**

system consists of only one phase

1. Solutions

phases consists of different types of molecules

2. Pure substances

phase consists of a single type of molecules

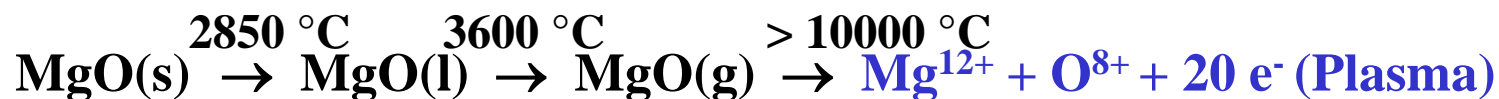
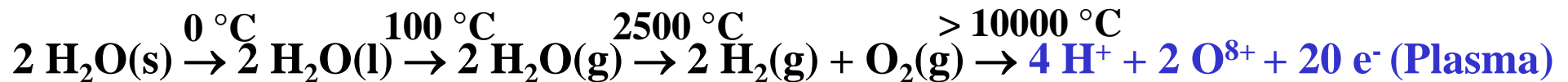
a. Compounds

mol. structure based on different types of atoms

b. Elements

mol. structure based on a single type of atoms

All substances can be cleaved into the corresponding elements through dissociation processes at sufficiently high temperatures:





# 3. Atoms and Molecules

## Contents

- 3.1 Law of mass preservation**
- 3.2 Law of constant proportions**
- 3.3 Law of multiple proportions**
- 3.4 Law of equivalent proportions**
- 3.5 Dalton's atom hypothesis**
- 3.6 Volume ratio during chemical reactions**
- 3.7 Relative mass of atoms**
- 3.8 Molar masses**
- 3.9 Absolute atomic masses**

# 3.1 Law of Mass Preservation

**During all Chemical Reactions the Total Mass of the Reactants Remains Constant**

**(Antoine Lavoisier 1774)**

**Experimental confirmation by thorough determination of the mass of the educts and products (Hans Landolt 1908)**

**⇒ change of mass < 10<sup>-5</sup>%**

**But: chemical reactions are subject to energy conversion  $\Delta E$**

**Energy/mass equivalent:**

$$E = mc^2 \quad \text{(Albert Einstein 1915)}$$

**Highly exothermic reaction:  $\Delta E = 500 \text{ kJ} \Rightarrow$  change of mass  $\sim 10^{-9}\%$**

**⇒ Change of mass during chemical reactions is beyond weighing accuracy (analytical balance  $\sim 0.1 \text{ mg}$ )**



# 3.2 Law of Constant Proportions

**The Mass Ratio of two Chemical Elements Reacting to one Compound is Constant**  
(Joseph Louis Proust 1799)

**Hoffman's decomposition apparatus:**

**Volume ratio**

**H/O = 2:1 (H<sub>2</sub>O)**

**Mass ratio**

**H/O = 1:7.936**

**Further examples for constant mass ratios**

**Fe/S = 1:0.57 (FeS)**

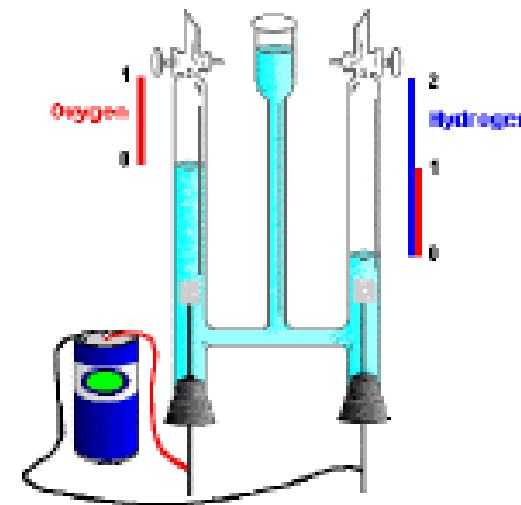
**Mg/O = 1:0.666 (MgO)**

**Na/Cl = 1:1.542 (NaCl)**

**H/N = 1:4.632 (NH<sub>3</sub>)**



**Water electrolysis**



# 3.3 Law of Multiple Proportions

The Mass Ratios of two Chemical Elements Reacting to one Compound are Related by an Integer Number

(John Dalton 1803)



## Examples for multiple mass ratios

Nitrogen oxides from  $N_2 + O_2 \rightarrow 2 NO \rightarrow NO_2 \dots$

- N/O = 1:0.571 = 1:1x0.571
- N/O = 1:1.142 = 1:2x0.571
- N/O = 1:1.713 = 1:3x0.571
- N/O = 1:2.284 = 1:4x0.571
- N/O = 1:2.855 = 1:5x0.571

## Carbon oxides

- C/O = 1:1.333 = 1:1x1.333
- C/O = 1:2.666 = 1:2x1.333

## Oxides known today

- |          |                             |
|----------|-----------------------------|
| $N_2O$   | <i>Dinitrogen monoxides</i> |
| $NO$     | <i>Nitrogen monoxide</i>    |
| $N_2O_3$ | <i>Dinitrogen trioxide</i>  |
| $NO_2$   | <i>Nitrogen dioxide</i>     |
| $N_2O_5$ | <i>Dinitrogen pentoxide</i> |
| $CO$     | <i>Carbon monoxide</i>      |
| $CO_2$   | <i>Carbon dioxide</i>       |

# 3.4 Law of Equivalent Proportions

**Elements are United to Chemical Compounds with Respect to Certain Masses or integer Multiples thereof (Jeremia Benjamin Richter 1791)**

By comparison of the mass ratios of nitrogen and oxygen in known nitrogen oxides with the corresponding ratios for the reaction of oxygen or nitrogen with hydrogen, it became clear that they only can be synthesized in certain integer ratios

## Nitrogen oxides, again

				$\text{NH}_3 : \text{H}_2\text{O}$	
1.	N/O	=	1:0.571	=	$(3 \times 4.632) : (1 \times 7.936) \sim 1.0 \text{ N} : 0.5 \text{ O}$
2.	N/O	=	1:1.142	=	$(3 \times 4.632) : (2 \times 7.936) \sim 1.0 \text{ N} : 1.0 \text{ O}$
3.	N/O	=	1:1.713	=	$(3 \times 4.632) : (3 \times 7.936) \sim 1.0 \text{ N} : 1.5 \text{ O}$
4.	N/O	=	1:2.284	=	$(3 \times 4.632) : (4 \times 7.936) \sim 1.0 \text{ N} : 2.0 \text{ O}$
5.	N/O	=	1:2.855	=	$(3 \times 4.632) : (5 \times 7.936) \sim 1.0 \text{ N} : 2.5 \text{ O}$

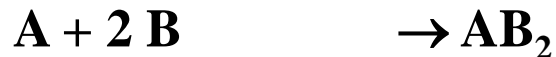
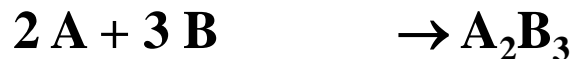
⇒ Concept of equivalent masses

⇒ Atomic masses and oxidation values

# 3.5 Dalton's Atom Hypothesis

## Atoms as elemental Structures of Matter (John Dalton 1808)

1. Elements cannot be split indefinitely, since they consist of tiny non-cleavable particles, the so-called atoms
2. All atoms of an element are of one sort (mass and shape)
3. Atoms of different elements possess different properties



etc.

**Relative atom masses cannot be measured directly as long as the exact ratio of the atoms in the newly formed compound is not know**

## 3.6 Volume Ratios During Chemical Reactions

### Observations Regarding Gases (Joseph Louis Gay-Lussac 1808)

Every quantity of a substance equals a certain gas volume at a certain pressure and temperature, if that quantity is gaseous or can be vaporized

Stoichiometric law of mass  $\Rightarrow$  law of volume

$\Rightarrow$  The volume ratio of two gaseous elements reacting to one chemical compound is constant and can be expressed by simple integer numbers

#### Examples

2 volumes of hydrogen + 1 volume of oxygen  $\rightarrow$  2 volumes of water vapour

1 volume of hydrogen + 1 volume of chlorine  $\rightarrow$  2 volumes of hydrogen chloride

## 3.7 Relative Atom Masses

**Relative Atom Masses Can Be Derived by Experimentally Determined Mass Ratios During Chemical Reactions (See Chapter 3.2)**

Mass ratios in water:

$$\text{H/O} = 1:7.936$$

Ratio of atomic numbers in water:

$$\text{H}_2\text{O} \Rightarrow 1 \text{ O} = 15.872 \text{ H}$$

Definition of a point of reference needed:

The carbon isotope  $^{12}\text{C}$  was chosen by IUPAC in 1961 to be the reference point and exhibits a relative atom mass  $A_r = 12.000$

<u>Element</u>	<u>Rel. atom mass <math>A_r</math></u>
Hydrogen	1.008 u
Chlorine	35.453 u
Oxygen	15.999 u
Nitrogen	14.007 u
Carbon	12.011 u

**Definition of the atomic mass unit:**

$$1 \text{ u} = 1/12 m (^{12}\text{C}\text{-atom})$$

**Elements consist of a number of isotopes!**

**Carbon for example also contains  $^{13}\text{C}$  and  $^{14}\text{C}$**

$$A_r (\text{C}) > 12$$



# 3.8 Molar Masses

**The Amount of an Element in Gram, which equals to the numerical Value of the relative Atom, always contains the same Number of Atoms, i.e.  $N_A$  Atoms**

**The mass of one mole of a substance is called the molar mass,  $M$ . The amount of that substance is thus given by:**

$$n = m/M$$

**The corresponding particle count is:**

$$N = n \cdot N_A$$

**$M$  = Molar mass [g/mol]**

**$m$  = Mass [g]**

**$n$  = Amount of substance [mol]**

**$N_A$  = Avogadro-constant [particles/mol]**

**$N$  = Particle count**

**Calculation of molar masses:**

$$M(\text{H}_2\text{O}) = 2 M(\text{H}) + M(\text{O}) = 2 \cdot 1.008 \text{ g/mol} + 15.999 \text{ g/mol} = 18.015 \text{ g/mol}$$

$$M(\text{CO}_2) = M(\text{C}) + 2 M(\text{O}) = 12.011 \text{ g/mol} + 2 \cdot 15.999 \text{ g/mol} = 44.009 \text{ g/mol}$$

# 3.9 Absolute Atom Masses

The absolute Atom Masses are given by the Division of the Molar Mass by the Avogadro Constant,  $N_A$

Determination of the Avogadro-constant necessary

$$\text{Density } \rho = \frac{m}{V} = \frac{4M(\text{Cu})}{N_A a^3} = 8.93 \text{ gcm}^{-3}$$

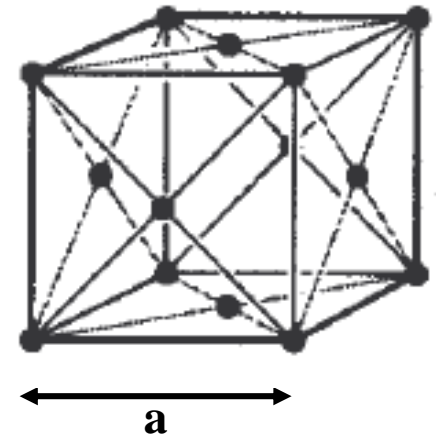
$$\Rightarrow N_A = \frac{4M(\text{Cu})}{\rho a^3} = 6.02214 \cdot 10^{23} \text{ mol}^{-1}$$

$$a = \text{lattice constant of Cu} = 3.62 \cdot 10^{-8} \text{ cm} = 3.62 \text{ \AA}$$

## Example

$$\begin{aligned} m(^{12}\text{C}) &= M(^{12}\text{C})/N_A \\ &= 12.0 \text{ g} \cdot \text{mol}^{-1} / N_A \\ &= 1.99269 \cdot 10^{-23} \text{ g} \end{aligned}$$

Unit cell of copper  
(cubic-face-centered)



## 3.9 Absolute Atom Masses

**The Absolute Atom Masses can be Calculated by Means of the Atomic Mass Unit, u**

Atomic mass unit

$$1 \text{ u} = 1/12 \cdot m(^{12}\text{C}) = 1.66054 \cdot 10^{-24} \text{ g}$$

<b>Element</b>	<b>Rel. atom mass <math>A_r</math></b>	<b>Molar mass [g/mol]</b>	<b>Abs. atom mass [<math>10^{-24}</math> g]</b>
<b>Hydrogen</b>	<b>1.008 u</b>	<b>1.008</b>	<b>1.678</b>
<b>Chlorine</b>	<b>35.453 u</b>	<b>35.453</b>	<b>58.871</b>
<b>Oxygen</b>	<b>15.999 u</b>	<b>15.999</b>	<b>26.567</b>
<b>Nitrogen</b>	<b>14.007 u</b>	<b>14.007</b>	<b>23.259</b>
<b>Carbon</b>	<b>12.011 u</b>	<b>12.011</b>	<b>19.945</b>

**In day-to-day life only relative atom and molecule masses or atom and molecule weights are used. Strictly speaking, the term weight is inadmissible, because weight is dependent on the gravitational field, in contrary to mass.**

# 4. The Atomic Structure

## Contents

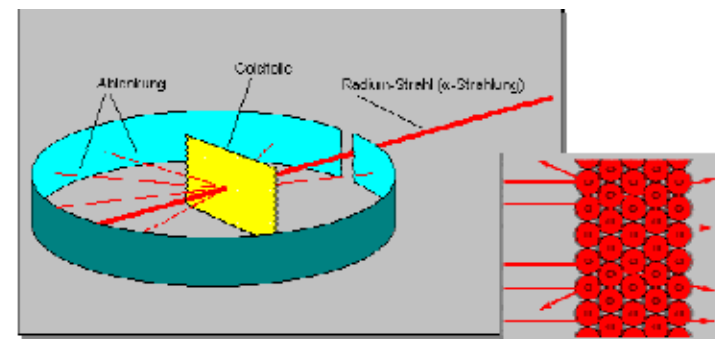
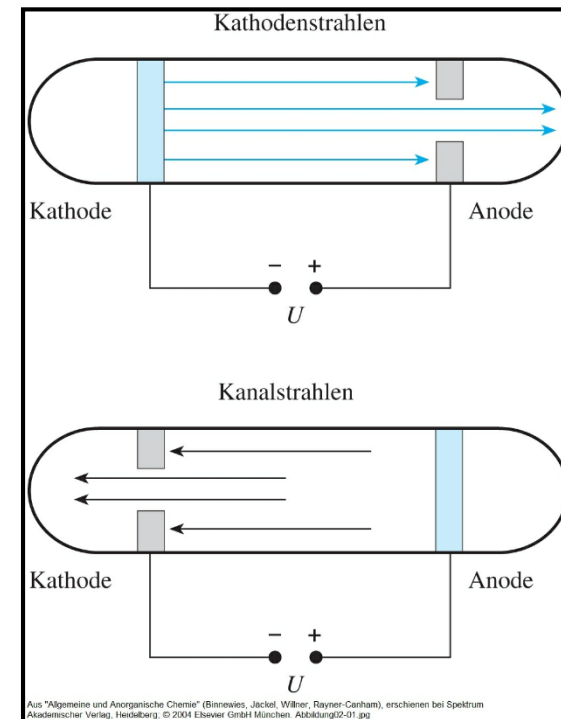
- 4.1 Fundamental Particles**
- 4.2 Atomic Nuclei and Chemical Elements**
- 4.3 Isotopes**
- 4.4 Mass Defect – Stability of Matter**
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- 4.6 Nuclear Reactions**
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- 4.8 Quantum Theory according to Planck**
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- 4.11 The Wave Character of Electrons**
- 4.12 Eigen Functions of the Schrödinger-Equation**
- 4.13 Quantum Numbers**
- 4.14 Energies of the Orbitals**
- 4.15 Structure of the Periodic Table**

# 4.1 Fundamental Particles

**Fundamental Particles are the smallest Building Blocks of Matter, which cannot be disassembled into smaller Components**

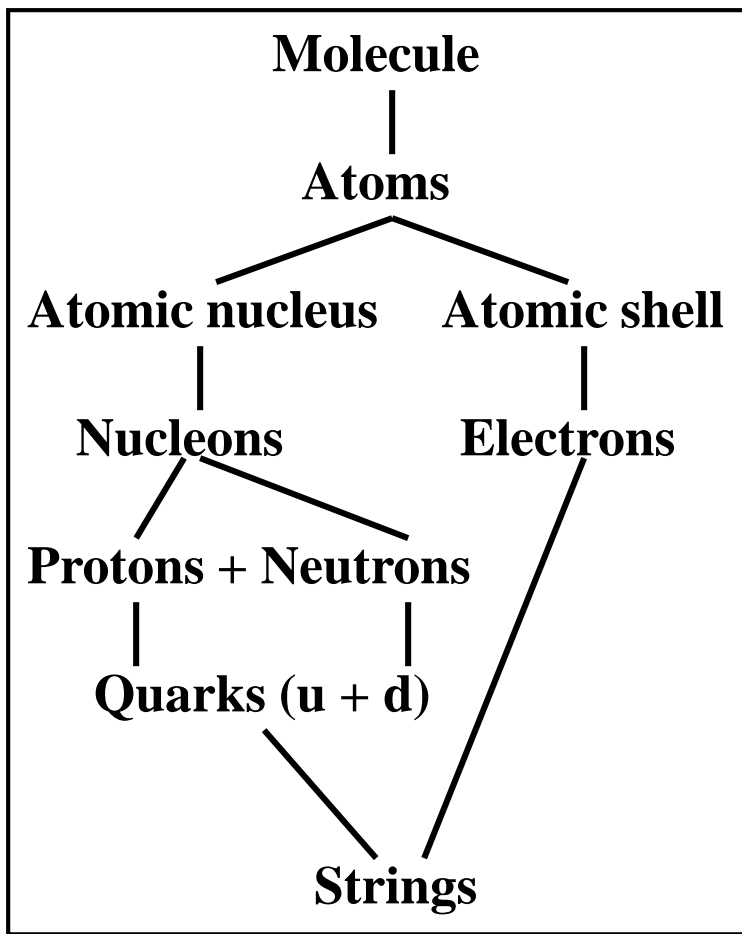
## Some historical discoveries of particle physics

1808	J. Dalton	Atomic hypothesis
1897	J.J. Thomson	Electrons + ions
1909	R.A. Millikan	Determination of unit charge
1913	E. Rutherford	Proton
1932	J. Chadwick	Neutron
1934	W. Pauli	Neutrino-Postulate ( $\beta$ -decay)
1940		Mesons, baryons
⋮		(cosmic radiation +
1970		particle accelerator)
1964	M. Gell-Mann	Quark-postulate
1995	Fermi-Lab	Detection of Top-quark
2013	CERN/LHC	Exp. proof of Higgs-Boson



# 4.1 Fundamental Particles

## Structure of Matter



## Properties of atomic building blocks

Particle	Electron	Proton	Neutron
Symbol	e	p	n
Mass	$0.9109 \cdot 10^{-27}$ g 0.51 MeV	$1.6725 \cdot 10^{-24}$ g 938.27 MeV	$1.6725 \cdot 10^{-24}$ g 939.55 MeV
Charge	-e $-1.602 \cdot 10^{-19}$ C	+e $1.602 \cdot 10^{-19}$ C	0 0

Unit charge  $e = 1.602 \cdot 10^{-19}$  C

Mass can also be expressed in terms of energy by

$E = mc^2$  with  $1 \text{ eV} = 1.602 \cdot 10^{-19}$  J

or  $1 \text{ MeV} = 1.602 \cdot 10^{-13}$  J

# 4.1 Fundamental Particles

## Standard Model of Particle Physics (Charge) (Spin)

Electron e 0.511 MeV, -e, 1/2	Myon $\mu$ 105.7 MeV, -e, 1/2	Tau $\tau$ 1777 MeV, -e, 1/2
Electron-Neutrino $\nu_e$ < 2.2 eV, 0, 1/2	Myon-Neutrino $\nu_\mu$ < 0.17 MeV, 0, 1/2	Tau-Neutrino $\nu_\tau$ < 15.5 MeV, 0, 1/2
Up u 2.4 MeV, +2/3 e, 1/2	Charme c 1270 MeV, +2/3 e, 1/2	Top t 171200 MeV, +2/3 e, 1/2
Down d 4.8 MeV, -1/3 e, 1/2	Strange s 104 MeV, -1/3 e, 1/2	Bottom b 4200 MeV, -1/3 e, 1/2

Fermions =

Leptons +  
anti-leptons

Quarks +  
anti-quarks

Power	Strong nuclear power	<b>Electromagnetism</b>	Weak nuclear power	Gravitation
Carrier	Gluon	<b>Photon</b>	W- and Z-Boson	Graviton
Effect on	Quark	<b>Quarks and charged leptons</b>	Quarks and leptons	All particles
Responsible for	Cohesion of nucleons	<b>Chemistry, electricity, magnetism</b>	Radioactivity, nuclear fusion	Planetary systems, galaxy(cluster)

## 4.2 Atomic Cores and Chemical Elements

**A Chemical Element is Made up from Atomic Nuclei with the Same Number of Protons (Proton Number or Atomic Number Z)**

### Nomenclature

Mass number	E	Charge
Proton number		Atomic number

${}^1_1\text{H}$       1 Proton

${}^2_2\text{He}$       2 Protons

${}^3_3\text{Li}$       3 Protons

Sorts of atoms that can be exactly characterized by the number of protons and neutrons are called nuclides

${}^1_1\text{H} = 1$  Proton

${}^2_1\text{H} = 1$  Proton + 1 Neutron (deuterium)

${}^3_1\text{H} = 1$  Proton + 2 Neutrons (tritium)

${}^4_2\text{He} = 2$  Protons + 2 Neutrons

The charge of the atoms is defined by the number of electrons

Hydrogenium cation       $\text{H}^+ = 1$  Proton

Hydrogen atom       $\text{H} = 1$  Proton + 1 electron

Hydride anion       $\text{H}^- = 1$  Proton + 2 electrons



## 4.3 Isotopes

**Nuclides with the Same Number of Protons but Different Number of Neutrons are called Isotopes**

Atomic number	Element	Nuclide symbol	Number of protons	Number of neutrons	Nuclide mass	Fraction of atomic number
1	Hydrogen H	$^1\text{H}$	1	0	1.0078	99.985
		$^2\text{H}$	1	1	2.0141	0.015
		$^3\text{H}$	1	2		Traces
2	Helium	$^3\text{He}$	2	1	3.0160	0.00013
	He	$^4\text{He}$	2	2	4.0026	99.99987
3	Lithium	$^6\text{Li}$	3	3	6.0151	7.42
	Li	$^7\text{Li}$	3	4	7.0160	92.58
4	Beryllium Be	$^9\text{Be}$ (Pure element)	4	5	9.0122	100.0
5	Boron	$^{10}\text{B}$	5	5	10.0129	19.78
	B	$^{11}\text{B}$	5	6	11.0093	80.22
6	Carbon C	$^{12}\text{C}$	6	6	12.0000	98.89
		$^{13}\text{C}$	6	7	13.0034	1.11
		$^{14}\text{C}$	6	8		Traces

# 4.3 Isotopes

**The average atomic Mass of an Element can be Derived from the Atomic Masses of the Isotopes weighted by the natural Isotope Distribution**

$$A_r(\text{E}) = X_1 \cdot A_r(\text{N}_1) + X_2 \cdot A_r(\text{N}_2) + \dots + X_n \cdot A_r(\text{N}_n) \quad X_1 + X_2 + \dots + X_n = 1$$

$X_n$  = Atomic number fraction of nuclides  $\text{N}_n$

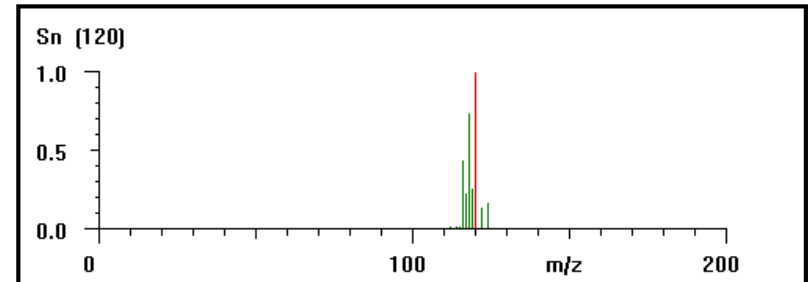
For carbon one derives:

$$A_r(\text{C}) = (98.89 \cdot 12.000 \text{ u} + 1.11 \cdot 13.0034 \text{ u}) / 100 = 12.011 \text{ u}$$

Most elements are mixed elements, whereas cores with 2, 8, 20, 28, 50, and 82 protons are particularly stable

⇒ High number of stable isotopes

⇒  $_{50}\text{Sn}$  Isotope:  $^{112}\text{Sn}$ ,  $^{114}\text{Sn}$ ,  $^{115}\text{Sn}$ ,  $^{116}\text{Sn}$ ,  $^{117}\text{Sn}$ ,  
 $^{118}\text{Sn}$ ,  $^{119}\text{Sn}$ ,  $^{120}\text{Sn}$ ,  $^{122}\text{Sn}$ ,  $^{124}\text{Sn}$



The distribution of isotopes in a mixed element strongly depends on the origin (location), since physical and geological processes can cause enrichment of isotopes  
⇒ Age determination, e.g. with help of amount of  $^{14}\text{C}$ )

# 4.4 Mass Defect – Stability of Matter

**The Mass of the Atomic Nuclei of all Nuclides is smaller than the Sum of the Masses of the individual Core Units (Mass Defect = Nuclear Binding Energy)**

**Example:  ${}^4\text{He}$ -cores**

**Calculated Mass =  $2\text{ p} + 2\text{ n} = 4.0319\text{ u}$**

**Experimentally found =  $4.0015\text{ u}$**

**Mass defect =  $0.0304\text{ u}$  ( $\sim 0.75\%$ )**

**Difference =  $E = mc^2$**

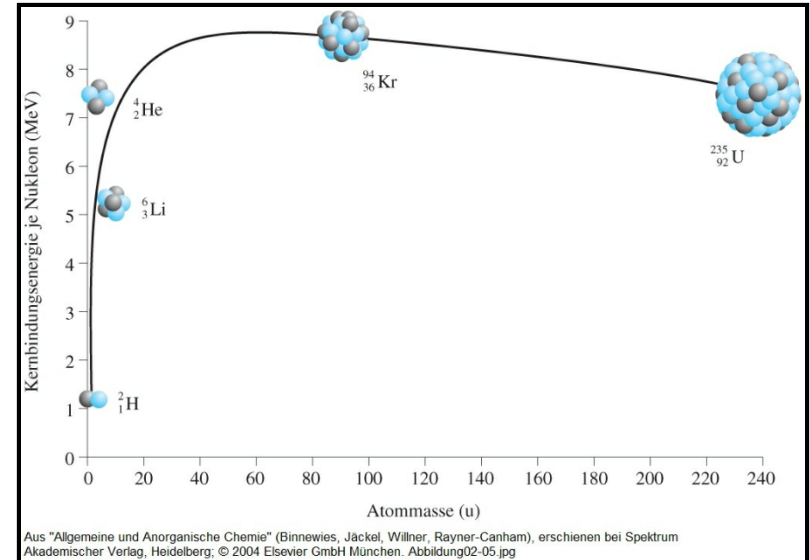
**$\Rightarrow$  The formation of  $4.0015\text{ g}$  He-cores from protons and neutrons yields ca.  $2.7 \cdot 10^9\text{ kJ}$**

**For comparison**

**$\text{C} + \text{O}_2 \rightarrow \text{CO}_2 + 393.77\text{ kJ/mol}$**

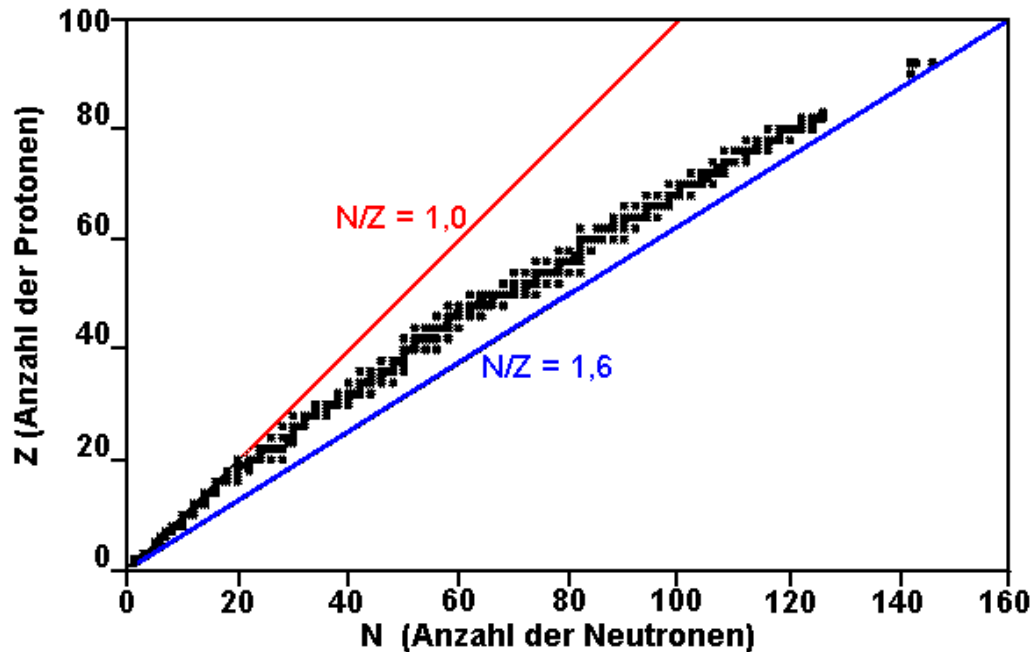
**$\Rightarrow$  For the production of  $2.7 \cdot 10^9\text{ kJ}$  of energy  $82.2\text{ t}$  of C must be burnt!**

**Fusion of core particles to atomic nucleus  $\Rightarrow$  nuclear fusion**



# 4.4 Mass Defect – Stability of Matter

**An increasing Number of Nucleons Leads to stronger Core Forces acting between Adjacent Nucleons**



Light atom cores  $N/Z \sim 1.0$

Heavy atom cores  $N/Z \sim 1.6$

An increasing number of protons, which repulsive interactions are fa-reaching and have an effect on all core protons, leads to a less strong cohesion of the nuclear building blocks. Above a certain number of protons atomic nuclei are thus not stable any more

⇒ Irradiation of core particles (e.g. He-cores) ⇒ Radioactivity

## 4.4 Mass Defect – Stability of Matter

**The Stability of the atomic Nucleus and Nucleons is due to the strong Nuclear Power, which counteracts the Repulsive Coulomb Power between the Protons**

**Range of the strong nuclear power  $\sim 10^{-15}$  m > repulsive Coulomb-power**

Particle	Half-life period $t_{1/2}$	Decay product	Core binding energy / Nucleon	Consequence
Electron	stable	-	-	elemental
Proton	$> 10^{31}$ a	$\gamma$ -radiation	-	Non-elemental
Neutron	10.4 min	$p + e + \nu_e$	-	free neutrons do not exist
$^{56}\text{Fe}$ -core	stable	-	8.8 MeV = maximum	Nuclear fusion till Fe yields energy
$^{238}\text{U}$ -core	$4.5 \cdot 10^9$ a	$^{234}\text{Th} + ^4\text{He}$ ( $\alpha$ -radiation)	7.5 MeV	Nuclear fission yields energy

# 4.5 Radioactive Decay

**Radioactive Decay Processes obey first order Kinetics, i.e. the Number of Disintegrated Nuclei per Time Slot,  $dN/dt$ , is Proportional to the total Number of Nuclei Present,  $N$**

$$dN/dt = -k \cdot N \quad \text{with } k = \text{decay constant}$$

$$\Rightarrow dN/N = -k \cdot dt \quad \text{and } t = \text{time}$$



**Integration yields:**

$$\ln N - \ln N_0 = -k \cdot t$$

$$\Rightarrow \ln(N_0/N) = k \cdot t$$

**Half-life time  $t_{1/2}$ :  $N = N_0/2$**

$$\ln 2 = k \cdot t_{1/2}$$

$$t_{1/2} = (\ln 2)/k = 0.693/k$$

**Age determination**

**( $^{14}\text{C}$ -Methode)**

Neutronen aus Höhenstrahlung

$$^{14}_7\text{N} + ^1_0\text{n} \rightarrow ^{14}_6\text{C} + ^1_1\text{H}$$

$$^{14}_6\text{C} \xrightarrow{-\beta} ^{14}_7\text{N}$$

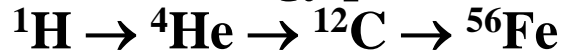
$t_{1/2} = 5568 \text{ Jahre}$

# 4.6 Nuclear Reactions

**Nuclear Reactions Represent the Primary Energy Source in the Cosmos and are Responsible for the Formation of the Elements**

## Nuclear fusion

- Stellar energy production



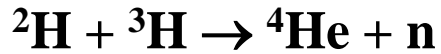
Sun converts 4 mill. t mass/s into energy  $\sim m(\text{Cheops})$

- Supernova explosions

r-Prozess  $\rightarrow {}^{256}\text{Lr}$

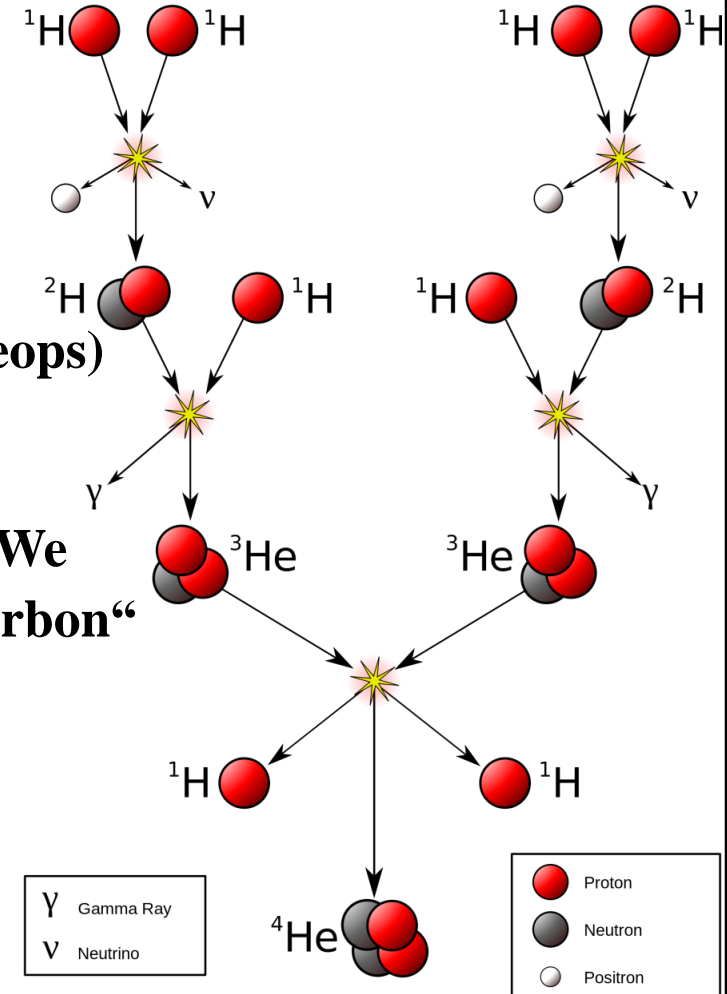
Song „Stardust“ von Crosby, Stills, Nash & Young: „We are stardust, we are golden, we are billion year old carbon“

- Thermonuclear weapons



Test on Bikini atoll

(H-Bomb Bravo 1954)



# 4.6 Nuclear Reactions

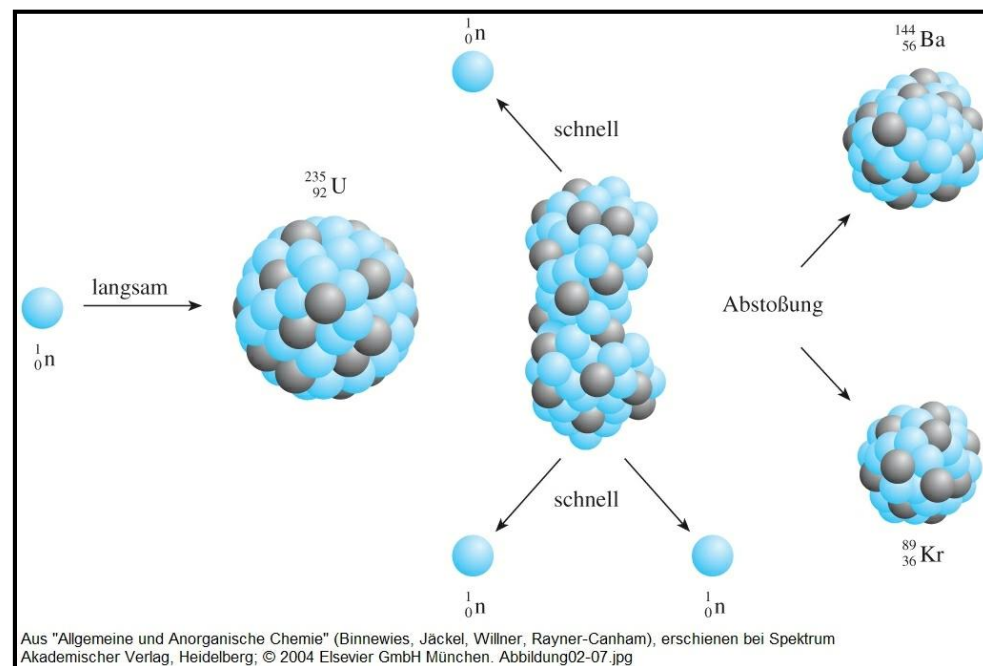
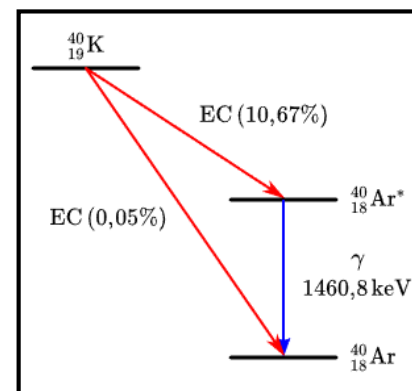
## Nuclear Reactions as Fission are used for electrical Energy Production

### Nuclear Fission

- Earth's warmth ( $^{238}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{40}\text{K}$ )  $\rightarrow$  geothermal energy, plate tectonics, Argon release, and volcanism

- Nuclear weapons ( $^{235}\text{U}$ ,  $^{239}\text{Pu}$ )
- Nuclear power stations ( $^{235}\text{U}$ ,  $^{239}\text{Pu}$ )  
$$^{235}\text{U} + \text{n} \rightarrow ^{90}\text{Kr} + ^{144}\text{Ba} + 2\text{n}$$

1 g  $^{235}\text{U}$  yields  $8.1 \cdot 10^7$  kJ, which equals to the energy released by combustion of 2.4 t Carbon





# 4.7 Origin and Abundance of the Elements

**All Elements heavier than Hydrogen are formed due to Nuclear Fusion**

## Big Bang

$> 10^{10} \text{ K} \Rightarrow 90\% \text{ H, } 10\% \text{ He}$

## Stars

$> 1 \cdot 10^7 \text{ K} \Rightarrow$  Fusion of hydrogen  $4 \text{ } ^1\text{H} \rightarrow \text{}^4\text{He} + 2 \text{ e}^+ + \nu_{\text{e}} + 26.72 \text{ MeV}$

$> 1 \cdot 10^8 \text{ K} \Rightarrow$  Fusion of helium  $3 \text{ } ^4\text{He} \rightarrow \text{}^{12}\text{C} + \gamma + 7.28 \text{ MeV}$

$> 5 \cdot 10^8 \text{ K} \Rightarrow$  Fusion of carbon  $\text{}^{12}\text{C} + \text{}^4\text{He} \rightarrow \text{}^{16}\text{O} + \gamma + 7.15 \text{ MeV}$

$\text{}^{16}\text{O} + \text{}^4\text{He} \rightarrow \text{}^{20}\text{Ne} + \gamma + 4.75 \text{ MeV}$

..... till  $\text{}^{56}\text{Fe}$  (nucleus of lowest energy)

## Supernovae

$> 3 \cdot 10^9 \text{ K} \Rightarrow$  Formation of heavier elements until  $\text{}^{256}\text{Lr}$

(Observed at 1054 by Chinese, 1572 by Tycho Brahe, 1604 by Johannes Kepler)

**Today: Distribution of the elements in cosmos is 88.6% H, 11.3% He, 0.1% “metals“**

# 4.7 Origin and Abundance of the Elements

**The Probability Distribution of the Elements in terrestrial Atmos-, Bio-, Hydro-, Kryo- and Lithosphere is completely different to that in the Universe**

**Cause: Process of differentiation**

## 1. Formation of planetary systems

**Centre: sun with H and He**

**Periphery: planets and moons with H, He and “metallic dust”**

## 2. Formation of planets

**inner planets: small with low gravity  $\Rightarrow$  elements  $>$  Li**

**Core: heavy elements  $\Rightarrow$  Fe, Ni and other metals**

**Crust: light elements  $\Rightarrow$  silicates, aluminosilicates**

**outer planets: large with high gravity  $\Rightarrow$  light elements: H, He, CH<sub>4</sub>, NH<sub>3</sub>....**

## 3. Evolution of planetary atmosphere (primordial $\rightarrow$ today's atmosphere)

**Venus: CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O**

**CO<sub>2</sub>/N<sub>2</sub>**

**H<sub>2</sub>O(g)  $\rightarrow$  2 H $\uparrow$  + O $\uparrow$**

**Earth: CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O**

**N<sub>2</sub>/O<sub>2</sub>/Ar**

**CO<sub>2</sub>  $\rightarrow$  carbonates $\downarrow$**

**CO<sub>2</sub>  $\rightarrow$  C + O<sub>2</sub> (biol. active)**

**H<sub>2</sub>O(g)  $\rightarrow$  H<sub>2</sub>O(l) (oceans)**

**Mars: CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O**

**CO<sub>2</sub>/N<sub>2</sub>**

**H<sub>2</sub>O(g)  $\rightarrow$  H<sub>2</sub>O(s) $\downarrow$**



## 4.7 Origin and Abundance of the Elements

### Abundance of Elements in Earth's Shell (Atmos-, Bio-, Hydro-, Kryo- and Lithosphere) in Weight Percentage

Abundance [%]	Element(s)
48.9	O
26.3	Si
10 - 1	Al, Fe, Ca, Na, K, Mg
1 – 0.1 (1‰)	H, Ti, Cl, P
0.1 – 0.01	Mn, F, Ba, Sr, S, C, N, Zr, Cr
0.01 - 10 <sup>-3</sup>	Rb, Ni, Zn, Ce, Cu, Y, La, Nd, Co, Sc, Li, Nb, Ga, Pb, Th, B
10 <sup>-3</sup> - 10 <sup>-4</sup> (1 ppm)	Pr, Br, Sm, Gd, Ar, Yb, Cs, Dy, Hf, Er, Be, Xe, Ta, Sn, U, As, W, Mo, Ge, Ho, Eu
10 <sup>-4</sup> – 10 <sup>-5</sup>	Tb, I, Tl, Tm, Lu, Sb, Cd, Bi, In
< 10 <sup>-5</sup>	Hg, Ag, Se, Ru, Te, Pd, Pt, Rh, Os, Ne, He, Au, Re, Ir, Kr....

From left to right with decreasing probability (A.F. Hollemann, N. Wiberg)

# 4.8 Quantum Theory According to Planck

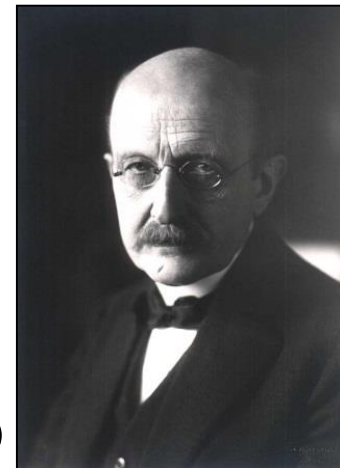
**Electromagnetic Radiation is Described as a Particle Flux, whereby the Energy of a Particle cannot be arbitrary, but must be a Multiple of a Quantum (Smallest Energy Value) (Max Planck 1900)**

$$E = h\nu$$

with  $h = 6.626 \cdot 10^{-34}$  Js (Planck's constant)  
and  $\nu$  = frequency [ $s^{-1}$ ]

$$E = hc/\lambda$$

Speed of light:  $c = \lambda\nu = 2.9979 \cdot 10^8$  ms $^{-1}$   
(1 s ~ 30 cm, 1 y ~  $1 \cdot 10^{13}$  km, 13.8 Gy ~  $13.8 \cdot 10^{22}$  km)



The energy of a light quantum (photons) is proportional to the frequency or anti-proportional to the wavelength

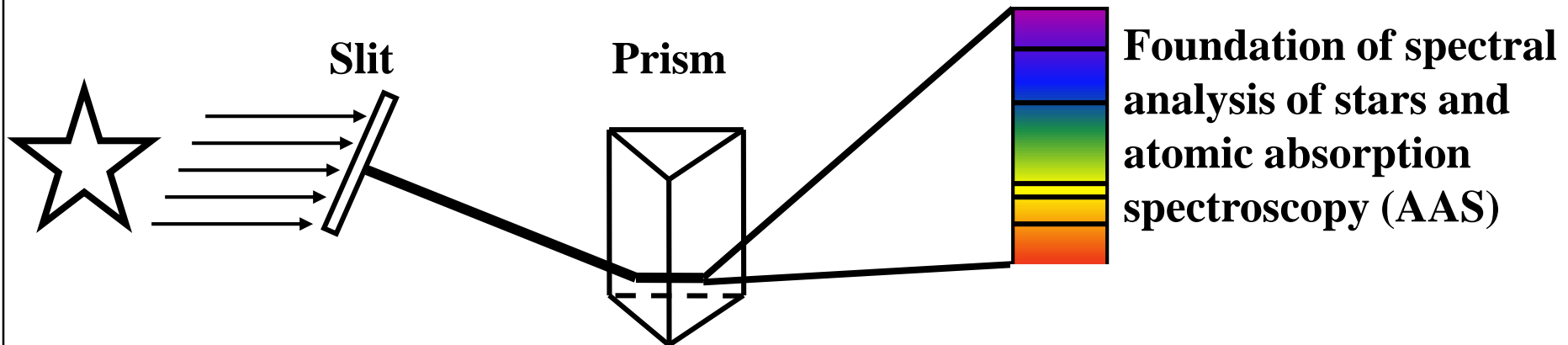
Calculation of the number of photons for 1 W (1 Js $^{-1}$ ) optical photons at 550 nm

Energy of a photon:  $E = hc/\lambda = hc/550 \cdot 10^{-9}$  m =  $4 \cdot 10^{-19}$  J per photon

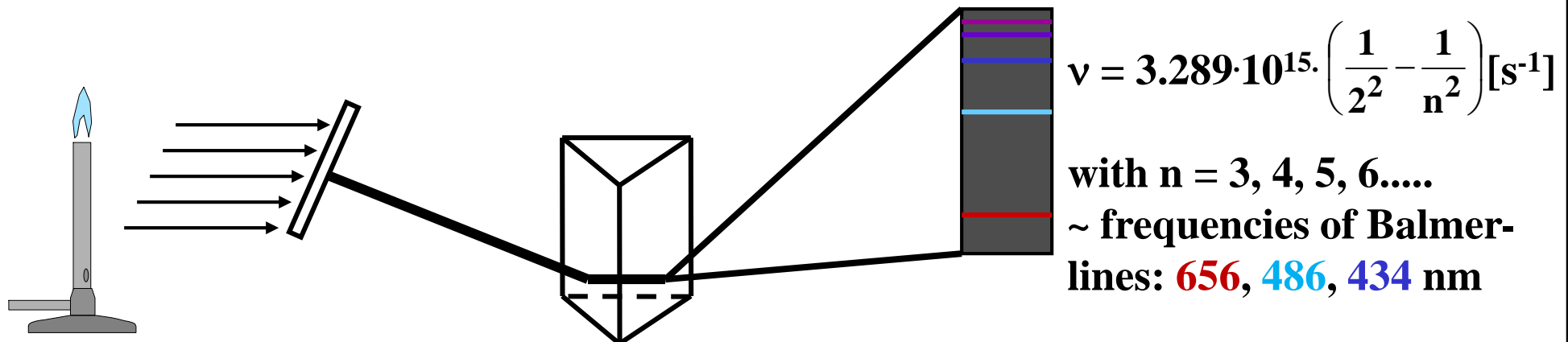
⇒ Number of photons: Total energy/energy of a photon  
 $= 1 \text{ Js}^{-1} / 4 \cdot 10^{-19} \text{ J} = 2.5 \cdot 10^{18} \text{ photons s}^{-1} \sim 4.2 \text{ } \mu\text{mol photons}$

# 4.9 Atomic Spectra

**During the Splitting of Light discrete Absorption and Emission Lines occur in the Spectrum (characteristic Lines for every Elements)**



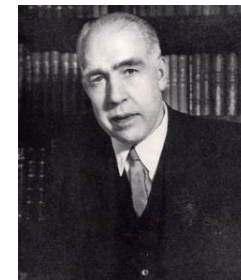
Solar or stellar light ⇒ Fraunhofer-Lines (Joseph von Fraunhofer 1820)



Hydrogen burner ⇒ Emission lines (Johann Jakob Balmer 1885)

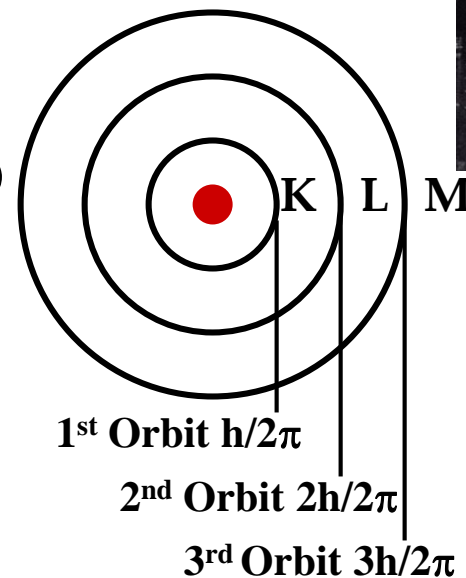
# 4.10 Bohr's Atomic Model

**First Attempt to describe the Electronic Shell of Atoms (Niels Bohr 1913)**



## Bohr's Model for the H-atom

- Nucleus much more heavy than electron ( $\Rightarrow$  at rest)
- Electron ( $m_e$ ,  $e$ ) circles around nucleus with an orbit radius,  $r$ , and an orbit velocity,  $v$
- Electron obeys centrifugal force:  $F_Z = m_e v^2/r$
- Electron is attracted by nucleus:  $F_{el} = e^2/4\pi\epsilon_0 r^2$
- For stable orbits:  $F_Z = -F_{el}$
- Radius of first orbit K:  $a_0 = 52.7$  pm



## Bohr's postulate

Not every orbit is allowed. Only orbits which orbital angular momentum,  $L = m \cdot r \cdot v$ , is a multiple,  $n$ , of the quantized angular momentum,  $h/2\pi$ , are stable

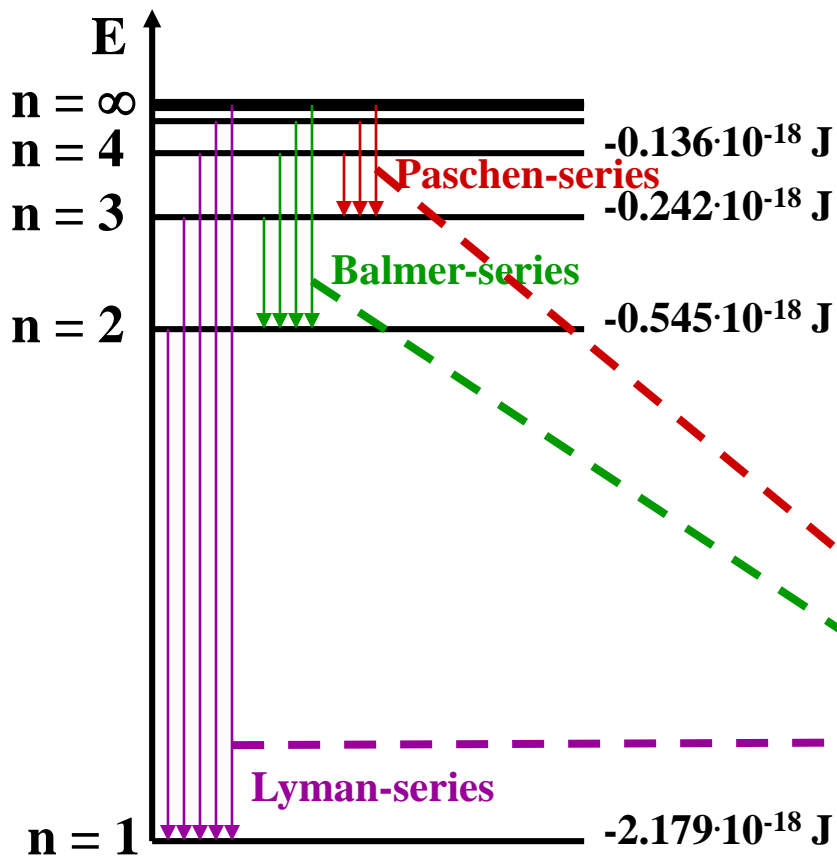
## Energy of the electron

$$E_n = - \frac{m e^4}{8 \epsilon_0 h^2} \cdot \frac{1}{n^2}$$
$$= -2.179 \cdot 10^{-18} / n^2 \text{ J}$$

with  $n = 1, 2, 3, \dots$

# 4.10 Bohr's Atomic Model

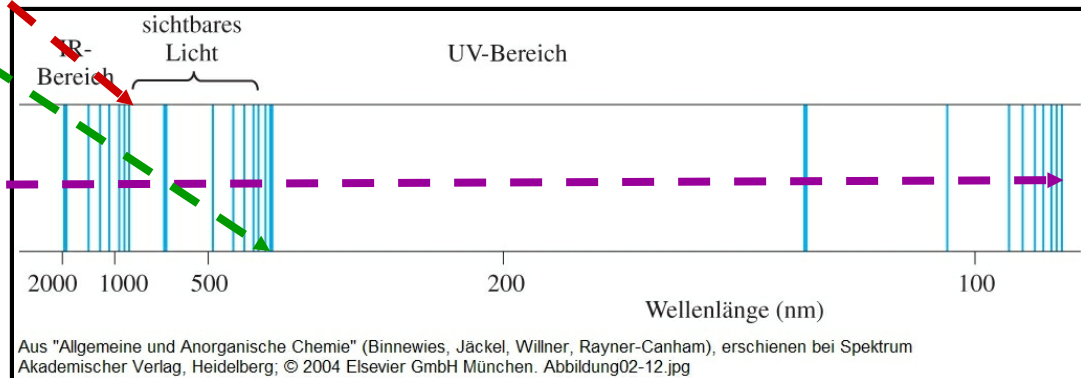
## Explanation of Line Spectrum of the H-Atom



$$\Delta E = h\nu = E_2 - E_1 = -2.179 \cdot 10^{-18} \cdot \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) [\text{J}]$$

$$\Rightarrow \nu = -\frac{2.179 \cdot 10^{-18}}{h} \cdot \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) [\text{s}^{-1}]$$

$$= 3.289 \cdot 10^{15} \cdot \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) [\text{s}^{-1}]$$



By Bohr's model solely atoms

with **a single electron** can be described properly, i.e. H, He<sup>+</sup>, Li<sup>2+</sup>, Be<sup>3+</sup>, and so on

# 4.11 The Wave Character of Electrons

**Any moving Particle exhibits Properties of a Wave Function (Louis deBroglie 1924)**

Linking  $E = hc/\lambda$  with  $E = mc^2$  leads to

$$\lambda = \frac{h}{mc}$$

deBroglie wavelength

Electrons on an orbit around the nucleus  
behave like a stationary wave  
(timely unchanged wave)

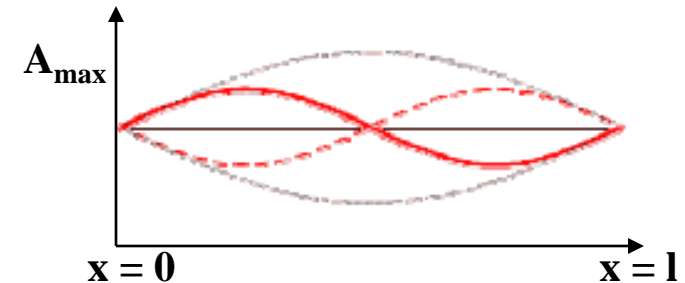
Prerequisites for a stationary wave

**Orbit:**  $n\lambda = 2\pi r$

$$\Rightarrow \frac{nh}{2\pi} = mvr$$

(Quantization of angular momentum)

Schwingende Saite



**String:** Amplitude  $A = 0$  for  $x = 0, 1$

$$\Rightarrow \lambda = 2l/n \text{ with } n = 0, 1, 2, 3$$

$$d^2(A(x))/dx^2 + 4\pi^2 v^2 A(x) = 0$$

$\Rightarrow$  Eigen-functions:

$$A(x) = A_{\max} \sin(2\pi vx + d)$$



# 4.11 The Wave Character of Electrons

**Electron Clouds are Three-Dimensional vibrating Systems with the possible vibrational States being represented by Three-Dimensional Stationary Waves**

Description of wave properties of electrons by **Erwin Schrödinger 1927**

$$\frac{\delta\Psi}{\delta x^2} + \frac{\delta\Psi}{\delta y^2} + \frac{\delta\Psi}{\delta z^2} + \frac{8\pi^2 m}{h^2} [E - V(x,y,z)] \cdot \Psi(x,y,z) = 0$$



- **Homogeneous differential equation of second order**
- **Solutions of wave functions  $\psi(x,y,z)$  are analogous to amplitude functions for the vibrating string**  
**E = energy, V = potential energy,**  
**m = mass of electron, h = Planck's quantum**
- **Wave functions are  $\psi(x,y,z)$  e-functions**

# 4.12 Eigen-Functions of the Schrödinger-Equation

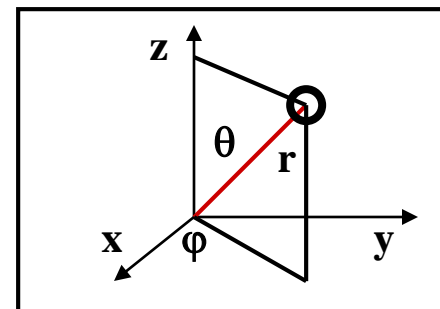
**The Solutions of a Differential Equation are so-called Eigen-Functions (in Case of the Schrödinger-Equations they are called Wave Functions)**

**Representation of polar coordinates  $r$ ,  $\theta$  and  $\varphi$**

**(analogous to longitude ( $\varphi$ ) and latitude ( $\theta$ ) in case of the globe)**

$$\Psi_{n,l,m}(r,\varphi,\theta) = R_{n,l}(r) \cdot \Theta_{l,m}(\theta) \cdot \Phi_m(\varphi)$$

*$n$ ,  $l$ ,  $m$  are indices  
for the wave  
functions*



- **The square of these functions describes the probability of an electron to be in a certain spot in a potential field, e.g. around an atomic nucleus**
- **$\psi^2_{n,l,m}$  = relative probability that the electron can be found at location  $(r,\varphi,\theta)$**
- **Prerequisite:  $\psi^2_{n,l,m}$  should be steady, unambiguously and finite**
- **Total probability:  $\psi^2_{n,l,m} dv \int 1$  (with  $v$  = volumes)**
- **The volume element, where the probability of presence of an electron is 95% is called atomic orbital**

# 4.12 Eigen-Functions of the Schrödinger-Equation

**s-Functions (s-Orbitals)  $n = 1, 2, 3, \dots$  and  $l, m = 0$  ( $a_0 = \text{Bohr Radius}$ )**

$$\Psi_{1s} = \Psi_{1,0,0} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \cdot e^{-r/a_0}$$

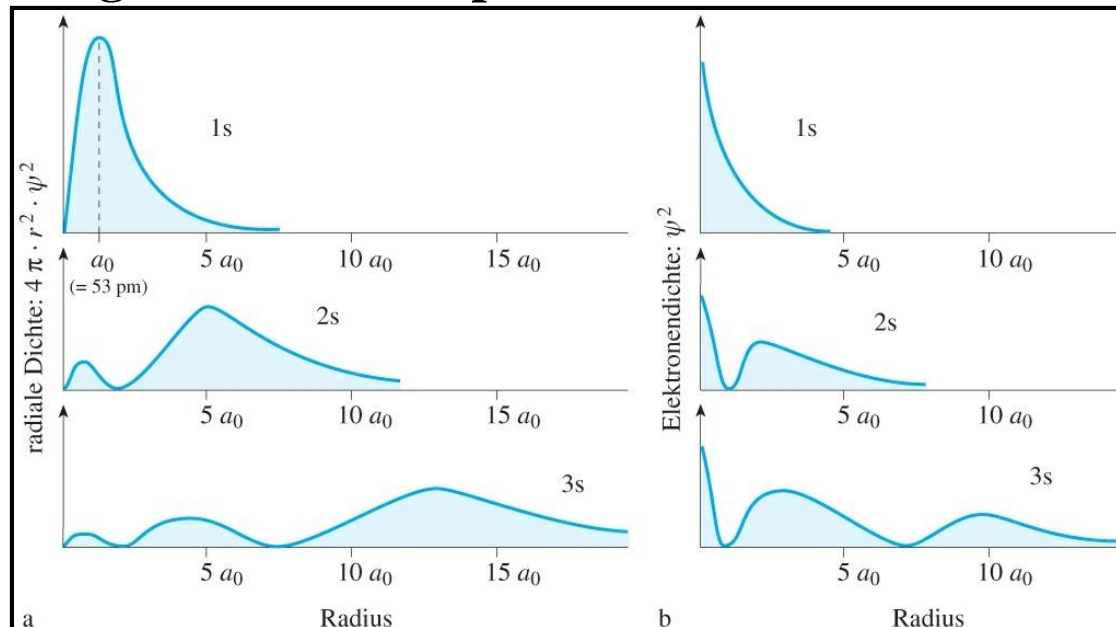
$$\Psi_{2s} = \Psi_{2,0,0} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \cdot (1 - r/a_0) e^{-r/2a_0}$$

- No angle-dependent part  $\Rightarrow$  rotationally symmetric
- No change of sign  $\Rightarrow$  no nodal plane

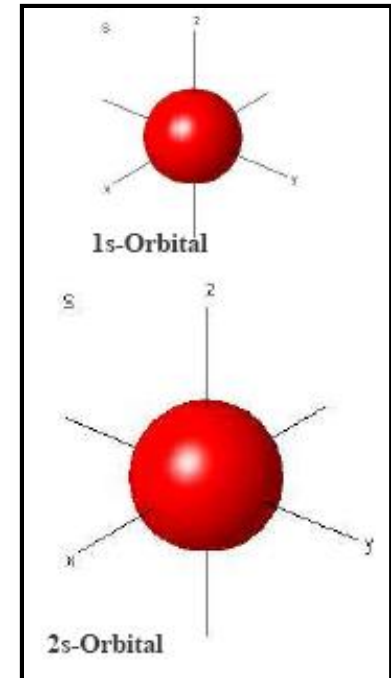
**1s Function**

**2s Function**

**3s Function**



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung02-16.jpg



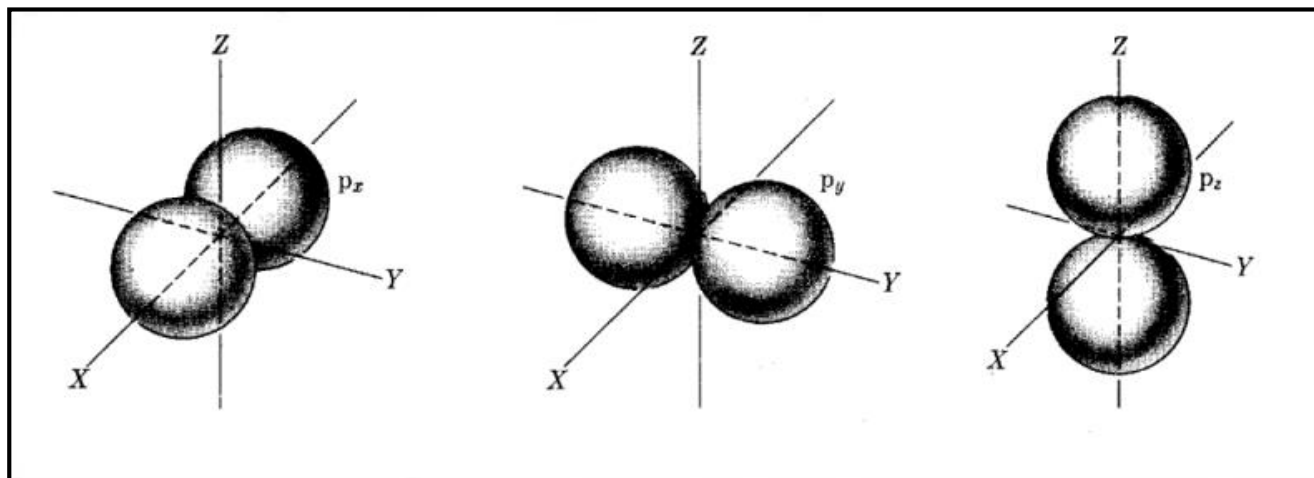
# 4.12 Eigen-Functions of the Schrödinger-Equation

**p-Functions (p-Orbitals)  $n = 2, 3, \dots$  and  $l = 1, m = -1, 0, 1$  ( $a_0 = \text{Bohr Radius}$ )**

$$\Psi_{2p_x} = \Psi_{2,1,1} = \frac{2}{\sqrt{3}} \left[ \left( \frac{1}{2a_0} \right)^{3/2} \cdot (r/2a_0) e^{-r/2a_0} \right] \left[ \frac{3}{2\sqrt{\pi}} \sin \theta \cos \varphi \right]$$

- **Angle-dependent part  $\Rightarrow$  not rotationally symmetric**
- **Change of sign  $\Rightarrow$  one nodal plane**

**Shape of orbitals with  $l = 1$  and all allowed  $n$**

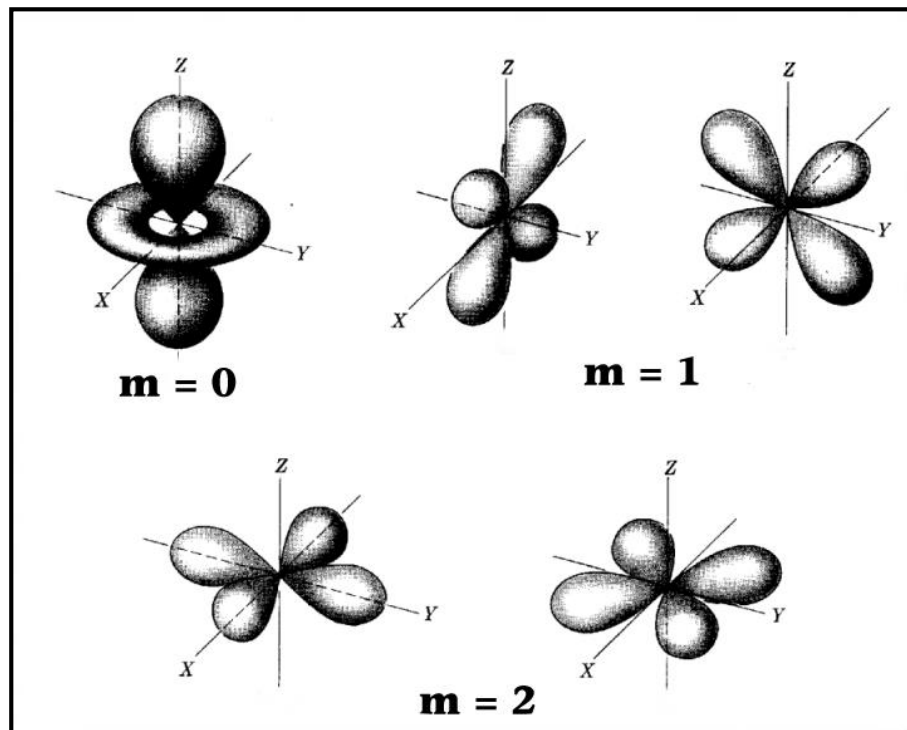


*During the transition to probability ranges the spheres are deformed to culls*

# 4.12 Eigen-Functions of the Schrödinger-Equation

## d-Functions (d-Orbitals) $n = 3, 4, \dots$ and $l = 2, m = -2, -1, 0, 1, 2$

- Angle-dependent part in two spatial dimensions  
⇒ more complex spatial distribution
- Two changes of sign ⇒ two nodal planes

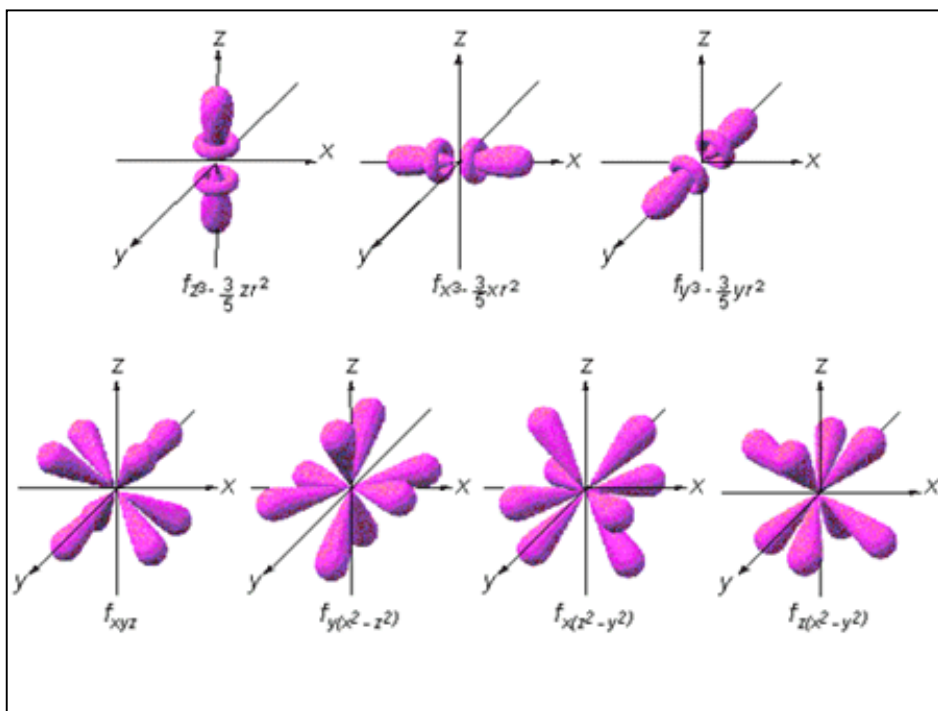


*During the transition to probability ranges the spheres are deformed again but the symmetry remains the same*

# 4.12 Eigen-Functions of the Schrödinger-Equation

## f-Functions (f-Orbitals) $n = 4, 5, \dots$ and $l = 3, m = -3, -2, -1, 0, 1, 2, 3$

- Angle-dependent part in three spatial dimensions  
⇒ even more complex spatial distribution
- Three changes of sign ⇒ three nodal planes



$m = 0$  and  $m = 1$

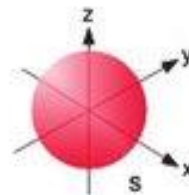
$m = 2$  and  $m = 3$

# 4.12 Eigen-Functions of the Schrödinger-Equation

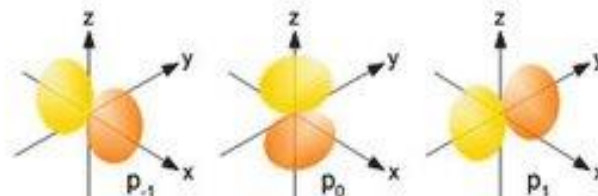
## Orbitals are Single Electron Wave Functions

**Orbital #**      **amount of nodal planes**

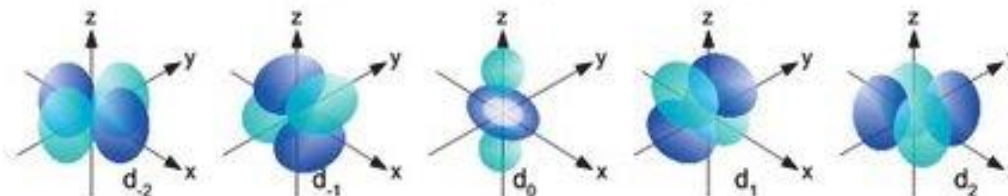
**s**      **1**      **0**



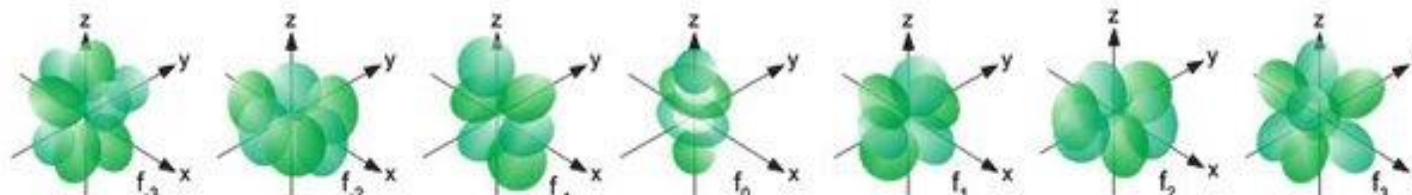
**p**      **3**      **1**



**d**      **5**      **2**



**f**      **7**      **3**

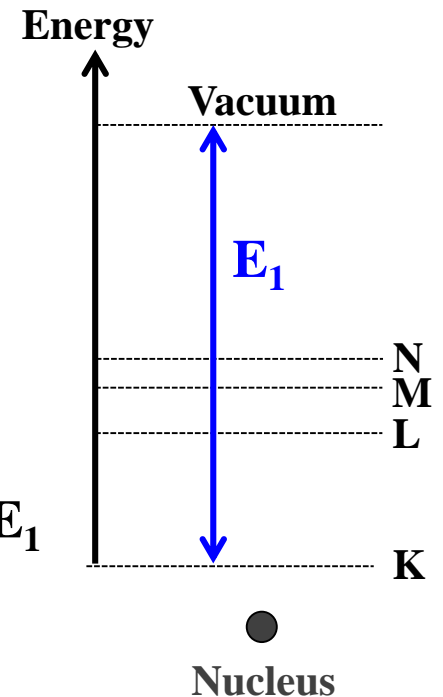


# 4.13 Quantum Numbers

**The three Indices as Solution Functions of the Schrödinger-Equation are called Quantum Numbers**

**The first quantum number, n, is called principal quantum number and defines the different main energy levels (shells) of the atoms (analogous to the orbits in Bohr's model)**

<b>Number</b>	<b>Denomination</b>	<b>Energy</b>
<b>n = 1</b>	<b>K-shell</b>	<b><math>E_1</math> (ground state)</b>
<b>n = 2</b>	<b>L-shell</b>	<b><math>1/4 E_1</math></b>
<b>n = 3</b>	<b>M-shell</b>	<b><math>1/9 E_1 + 1/4 E_1</math></b>
<b>n = 4</b>	<b>N-shell</b>	<b><math>1/16 E_1 + 1/9 E_1 + 1/4 E_1</math></b>
<b>n = 5</b>	<b>O-shell</b>	<b><math>1/25 E_1 + 1/16 E_1 + 1/9 E_1 + 1/4 E_1</math></b>
<b>.....</b>		





# 4.13 Quantum Numbers

**The second Quantum Number  $l$  is called Azimuthal or Orbital Quantum Number**

- It defines the different sub-energy levels (sub-shells) created due to orbital angular momentum
- Measurable through fine-splitting of spectral lines (if atomic emission spectra of high resolution are measured)

Shell	K	L	M	N
n	1	2	3	4
l	0	0 1	0 1 2	0 1 2 3
Term	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f

(Abbreviations are derived from spectroscopy: sharp, principal, diffuse, fundamental)

The following applies:  $l = 0, 1, 2, \dots, n-1$

orbital angular momentum:

$$L = \sqrt{l(l+1)} \frac{h}{2\pi}$$

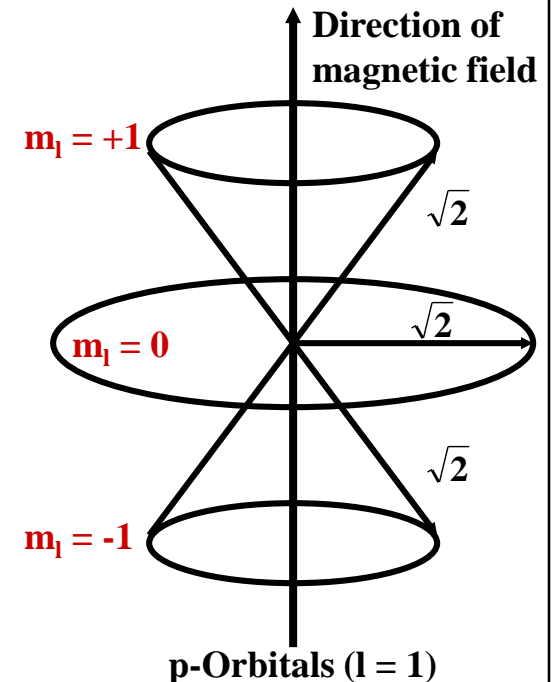
# 4.13 Quantum Numbers

The third Quantum Number,  $m_l$ , is called Magnetic Quantum Number, because in a Magnetic Field the Sub-Energy Levels can be discriminated

- The orbital angular momentum determined by the Azimuthal quantum number can only be oriented in certain quantized ways with reference to the magnetic field
- In spectroscopy, this splitting of spectral lines in a magnetic field is called Zeemann-effect

<u>l</u>	<u><math>m_l</math></u>	<u>Number of states</u>
0	0	1 s-state (orbital)
1	-1 0 +1	3 p-states (orbitals)
2	-2 -1 0 +1 +2	5 d-states (orbitals)
3	-3 -2 -1 0 +1 +2 +3	7 f-states (orbitals)

The following applies:  $m_l = -l \dots +l$



# 4.13 Quantum Numbers

**Die Spin Quantum Number,  $m_s$ , is the fourth Quantum Number Describing the Intrinsic Angular Momentum of the Electrons, which can Occupy two Orientations in a Magnetic Field**

- Both quantum states of the electron (spin orientations),  $m_s$ , are indicated by arrows:  $\uparrow m_s = +1/2$  (spin-up) or  $\downarrow m_s = -1/2$  (spin-down)

Shell	n	l	$m_l$	Number of orbitals	$m_s$	Number of e <sup>-</sup> -states	
K	1	0	0	1	$\pm 1/2$	2	2
L	2	0	0	1	$\pm 1/2$	2	8
		1	-1 0 +1	3	$\pm 1/2$	6	
M	3	0	0	1	$\pm 1/2$	2	14
		1	-1 0 +1	3	$\pm 1/2$	6	
		2	-2 -1 0 +1 +2	5	$\pm 1/2$	10	
N	4	0	0	1	$\pm 1/2$	2	32
		1	-1 0 +1	3	$\pm 1/2$	6	
		2	-2 -1 0 +1 +2	5	$\pm 1/2$	10	
		3	-3 -2 -1 0 +1 +2 +3	7	$\pm 1/2$	14	

# 4.14 Energy and Occupation of the Orbitals

## Atomic Orbitals of Hydrogen-Like Atoms (1 Electrons)

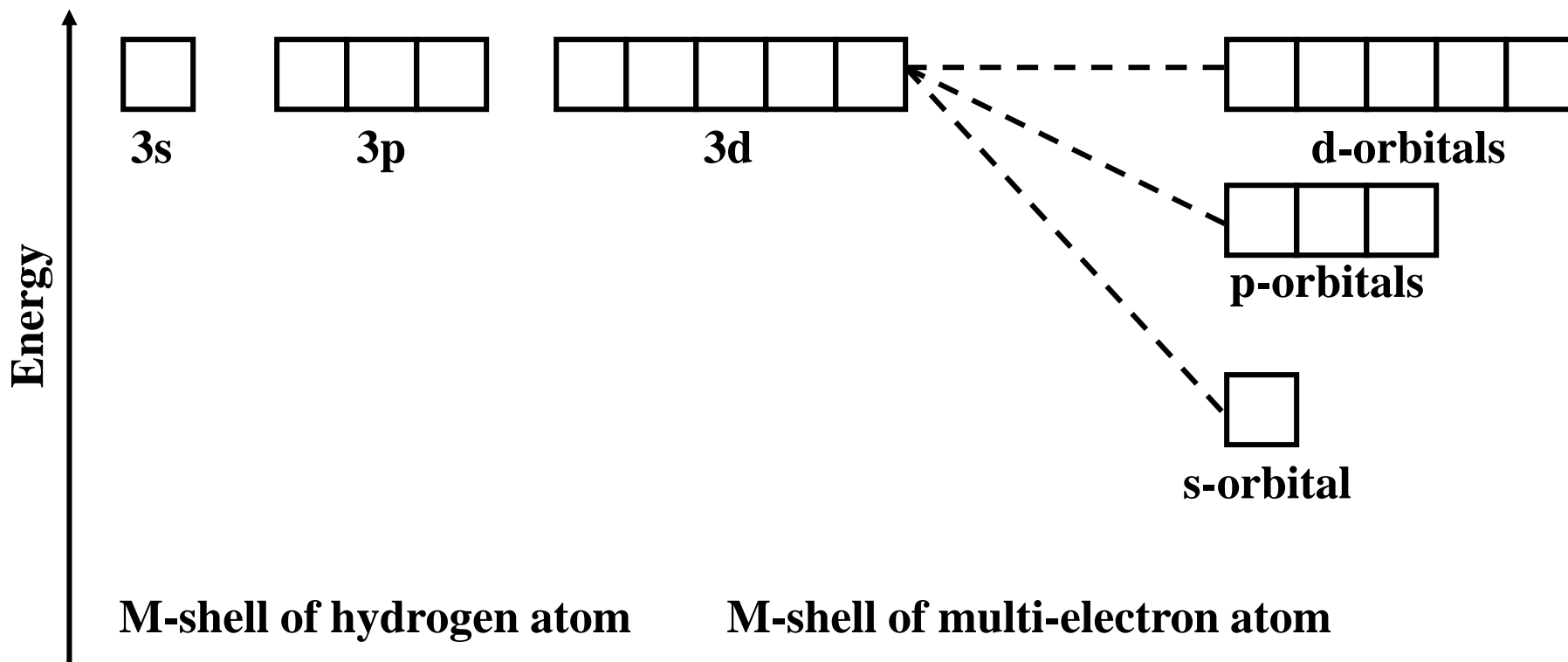
All orbitals of one shell possess the same energy (are degenerated)

Shell	n	s $l = 1$	p $l = 2$	d $l = 3$	f $l = 4$	Energy ↑
N	4	<input type="checkbox"/> 4s	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> 4p	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> 4d	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> 4f	
M	3	<input type="checkbox"/> 3s	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> 3p	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> 3d		
L	2	<input type="checkbox"/> 2s	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> 2p			
K	1	<input type="checkbox"/> 1s				

# 4.14 Energy and Occupation of the Orbitals

## Multi-Electron Atoms

Orbitals of one shell do not possess the same energy anymore (suspension of degeneracy through electron-electron interaction)



# 4.14 Energy and Occupation of the Orbitals

The Scheme for the Occupation of the Sub-Shells can be derived from the Dependencies of the Energy of the Sub-Shells on the Atomic Number

Shell

Q	7s	7p		
P	6s	6p	6d	
O	5s	5p	5d	5f
N	4s	4p	4d	4f
M	3s	3p	3d	
L	2s	2p		
K	1s			
	s	p	d	f

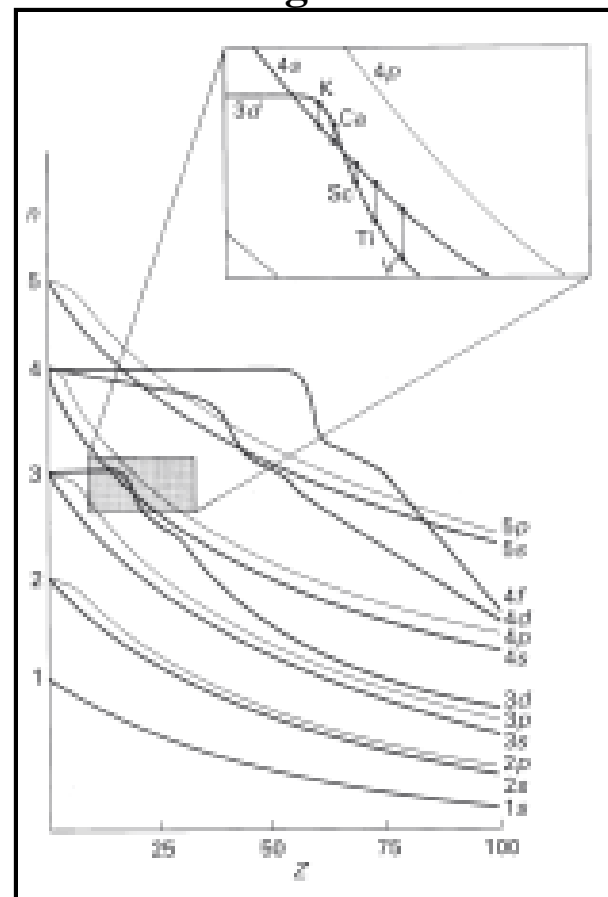
Sub-shell

Examples:

1s 2s 2p 3s 3p

1s 2s 2p 3s 3p 4s **3d** 4p 5s

Change of energy of the sub-shell with increasing atomic number



# 4.14 Energy and Occupation of the Orbitals

**The Occupation of States (Orbitals) by Electrons is prone to the Pauli Principle and Hund's Rule**

**Pauli-principle (W. Pauli, 1925)**

**In an atom two electrons cannot have the same 4 quantum numbers:**



Wolfgang Pauli



Friedrich Hund

**Hund's rules (F. Hund, 1927)**

**Degenerate, i.e. energetically equal, orbitals of the same type are occupied the way that the maximum number of unpaired electrons of the same spin is formed:**



**Lower energy**

**Higher energy → 2<sup>nd</sup> Hund's rule "state with highest L has lowest energy"**

# 4.15 Structure of the Periodic Table

**When the atomic Orbitals are filled with Electrons, periodic Changes are caused by Repetitions of the same electron arrangements on the outermost shell**

Atom	Orbital diagram	Electronic configuration	Group
H	$\boxed{\uparrow}$	$1s^1$	
He	$\boxed{\uparrow\downarrow}$	$1s^2$	[He] Noble gases
Li	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$	$1s^2 2s^1$	[He]2s <sup>1</sup> Alkaline metals
Be	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$	$1s^2 2s^2$	[He]2s <sup>2</sup> Alkaline earth metals
B	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\phantom{\uparrow}}$ $\boxed{\phantom{\uparrow}}$	$1s^2 2s^2 2p^1$	[He]2s <sup>2</sup> 2p <sup>1</sup> Boron group
C	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ $\boxed{\phantom{\uparrow}}$	$1s^2 2s^2 2p^2$	[He]2s <sup>2</sup> 2p <sup>2</sup> Carbon group
N	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$	$1s^2 2s^2 2p^3$	[He]2s <sup>2</sup> 2p <sup>3</sup> Nitrogen group
O	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$	$1s^2 2s^2 2p^4$	[He]2s <sup>2</sup> 2p <sup>4</sup> Chalcogens
F	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$	$1s^2 2s^2 2p^5$	[He]2s <sup>2</sup> 2p <sup>5</sup> Halides
Ne	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$	$1s^2 2s^2 2p^6$	[Ne] Noble gases
	1s      2s      2p		



# 4.15 Structure of the Periodic Table

1											13	14	15	16	17	18			
1												5	6	7	8	9	10	1	
H											B	C	N	O	F	Ne	2		
3	4											13	14	15	16	17	18	3	
Li	Be											Al	Si	P	S	Cl	Ar	4	
11	12	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	5	
Na	Mg	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	6	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	7	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	8	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	9	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	10	
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	11	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	12	
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	13	
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og	14	

58	59	60	61	62	63	64	65	66	67	68	69	70	71	
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	6
90	91	92	93	94	95	96	97	98	99	100	101	102	103	
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	7

Main group elements

Transition group elements (transition metals)

Lanthanides (rare earth metals)

Actinides (Actinium)

s- and p-block elements

d-block elements

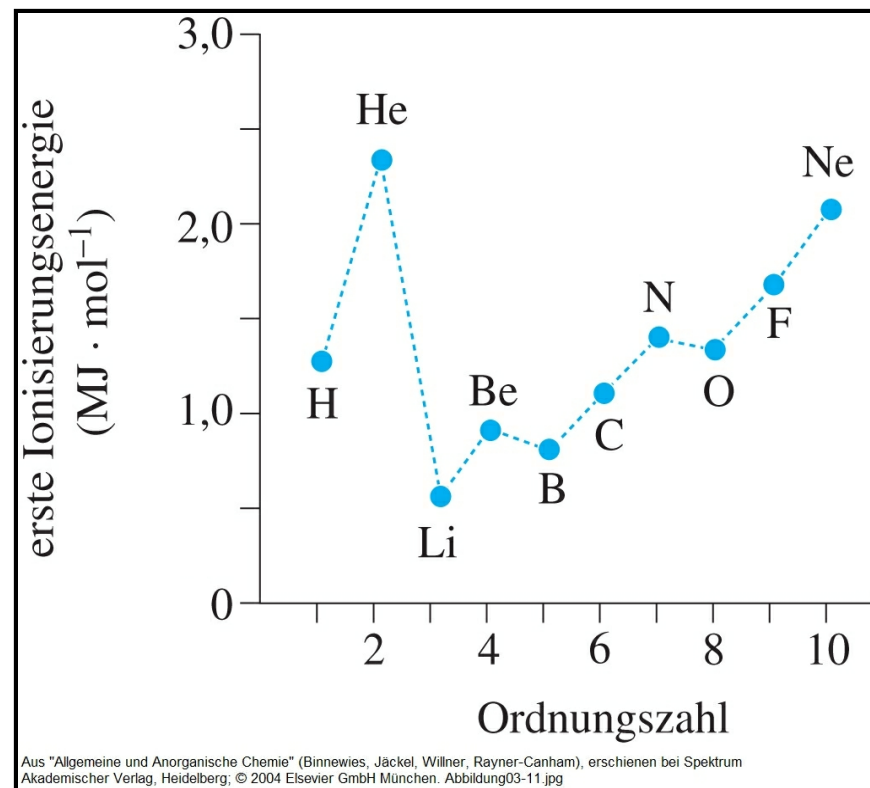
4f-block elements

5f-block elements

# 4.15 Structure of the Periodic Table

## Periodic Properties: Ionisation Energy

- **Ionisation energy,  $I$ , of an atom is the energy which is required to remove one electron from the highest occupied state:**  
 $A \rightarrow A + e^- : +I$
- **It is negative for all elements, i.e. it always requires energy to remove one electron**
- **It decreases within one group of the PT from top to bottom (increasing size and shielding)**
- **It increases within the periods of the PT with increasing ordinal number (but not monotonically)**



# 4.15 Structure of the Periodic Table

## Periodic Properties: Affinity to Electrons

- **Electron affinity,  $E_A$ , of an atom is the energy which is released if it takes up a single electron**  
 $A + e^- \rightarrow A^- : -E_A$
- **In most cases, energy is released during the addition of one electron**
- **It's quantity depends on the attraction of the nucleus and on the electron-electron repulsion**
- **For the addition of a second electron the required energy is always higher, i.e.  $E_A$  is positive**  
(Repulsion of  $e^-$  and  $A^-$ )

$E_A$  in  $\text{kJmol}^{-1}$

Li	Be	B	C	N	O	F	Ne
-66	-6	-33	-128	~0	-147	-334	-6
Na							
-59							
K							
-55							
Rb							
-53							
Cs							
-52							

# 5. Hydrogen

## Contents

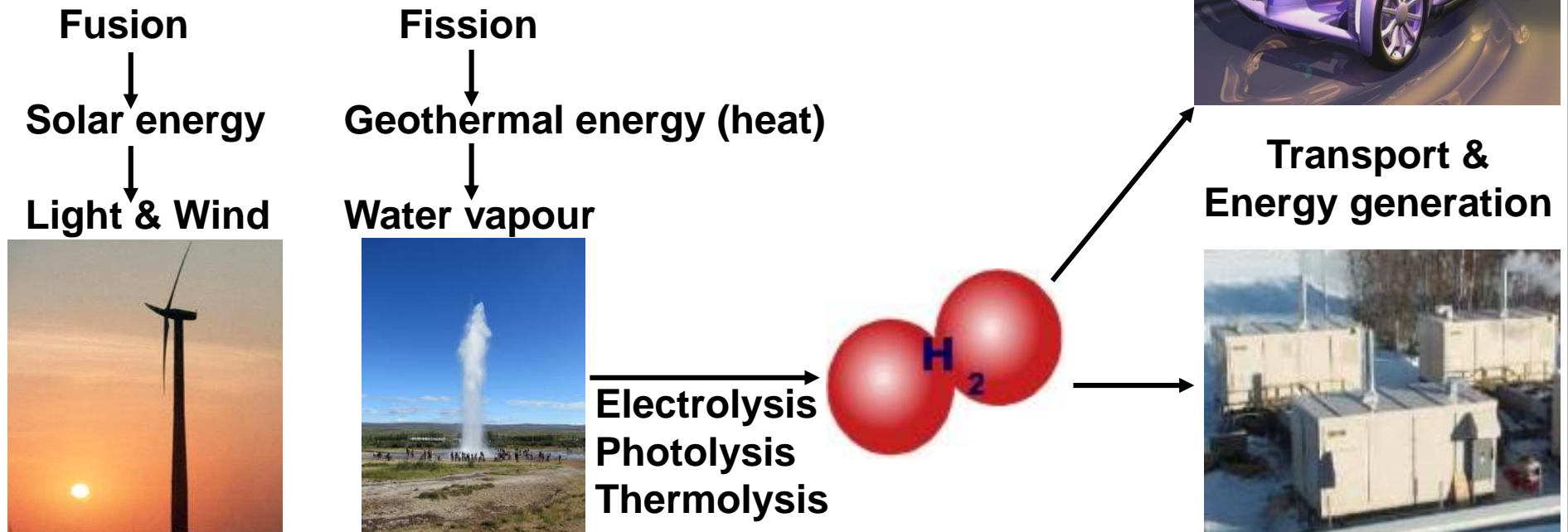
5.1 Isotopes and Physical Properties

5.2 Synthesis and Reactivity

5.3 Technical Application

5.4  $^1\text{H}$ -NMR Spectroscopy

5.5 Hydrogen Technology



# 5.1 Isotopes and Physical Properties

**Hydrogen is the most common Element in the Universe and the basic Fuel of the Stellar Energy Production (and of the Future Energy Cycle?)**

Isotope	Rel. occurrence	$T_b$	$T_m$ ( $N_2O$ )	$T_b(N_2O)$	Enrichment upon evaporation
$H_2$	99.985%	-253.5 °C	0.0 °C	100.0 °C	
$D_2$	0.015%	-249.2 °C	3.8 °C	101.4 °C	
$T_2$	$1 \cdot 10^{-15}\%$	-248.0 °C	4.5 °C	101.5 °C	

$D_2O/H_2O$ -ratio  $\longrightarrow$  *climate analysis in drilled ice cores*

- $H_2$  has a very low density under standard pressure (1 bar) of about 0.0899 g/l (air: 1.30 g/l)  $\Rightarrow$  balloons / zeppelins
- $H_2$  has a very high diffusion ability in many materials  $\Rightarrow$  Storage of large amounts in Pd possible



## 5.2 Synthesis and Reactivity

### Synthesis

- a) In the lab     $\text{Zn} + 2 \text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$                        $(2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2)$   
                       $\text{CaH}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2 \text{H}_2$                        $(2 \text{H}^- \rightarrow \text{H}_2 + 2 \text{e}^-)$
- b) Technical     $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$                       (Water electrolysis)  
                       $\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3 \text{H}_2 + \text{CO}$                       (Steam reforming)  
                       $\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}$                       (Coal hydrogenation)  
                       $\text{C}_n\text{H}_{2n+2} \rightarrow \text{C}_{n-1}\text{H}_{2n} + \text{H}_2 + \text{C}$                       (Cracking of carbohydrates)

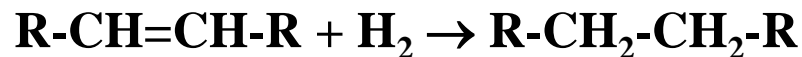
### Reactivity

- Molecular Hydrogen is rather inert at RT:  $\Delta H_{\text{dissociation}} = 436 \text{ kJ/mol}$
- Strongly exothermic oxyhydrogen gas reaction  $\text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$  has to be activated  $\Rightarrow T > 400 \text{ }^\circ\text{C}$ , UV radiation, sparks, Pt-catalyst, flash
- Atomic Hydrogen is highly reactive and reduces the oxides “of the half-noble“ metals, such as  $\text{CuO}$ ,  $\text{SnO}_2$ ,  $\text{PbO}$  and  $\text{Bi}_2\text{O}_3$  to the metals
- Formation of H-Atoms by microwaves, discharge, VUV radiation, or high temperature (9% of  $\text{H}_2$  dissociated at  $3000 \text{ }^\circ\text{C}$ )

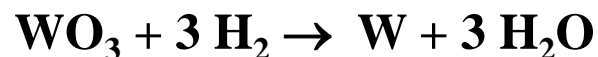
## 5.3 Technical Application

### Hydrogenation, Reductive Agent, Fuel, Ammonia Synthesis, Energy Storage

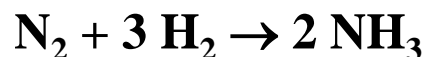
1. Hydrogenation of C=C bonds  $\Rightarrow$  hardening of plant oils (margarine)



2. Reductive agent  $\Rightarrow$  synthesis of metals



3. Ammonia synthesis  $\Rightarrow$  Haber-Bosch process



4. Fuel for space  $\Rightarrow$  space shuttle



5. Energy storage  $\Rightarrow$  hydrogen technology



# 5.4 Spectroscopy

## Hydrogen as an analyte

- **Astronomy**  
**21.11 cm Hydrogen line (1420.4 MHz)**  
**HI-Emission line in radio astronomy:**
  - Gas temperature
  - Magnet field strength
  - Structure and kinematik of galaxies/-cluster
- **Electrochemistry**  
**Normal Hydrogen Electrode (NHE)**
  - Reference electrode in CV, Coulometrie, ....
- **Biology/Chemistry**  
 **$^1\text{H}$ -NMR Spectroskopy (Nuclear spin  $I = \pm 1/2$ ):**
  - Structure solution
- **Medicine**  
**Nuclear spin resonance (MRT, T1-Relaxation)**
  - Imaging in medical diagnostics



# 5.4 $^1\text{H}$ -NMR Spectroscopy

**NMR Spectroscopy (Nuclear Magnetic Resonance) is applied for the Elucidation of Molecular Structures by Monitoring the Spin  $m_I$  of Nuclei, e.g. of Protons,  $p^+$**

## Principle

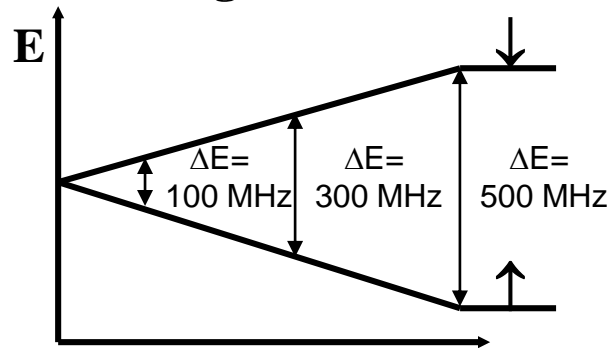
Protons ( $^1\text{H}$  nuclei) have a spin momentum as the electron has

$$\Rightarrow I = 1/2$$

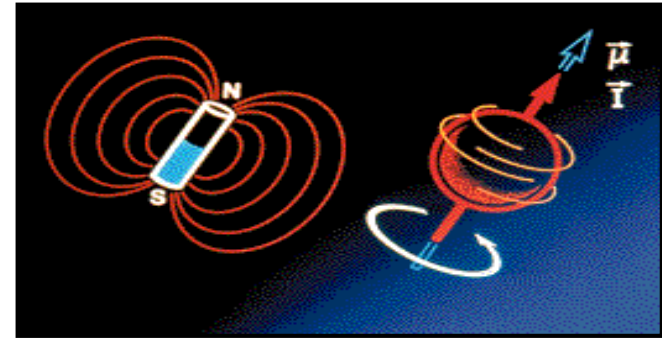
$$\Rightarrow 2 \text{ States: } m_I = +1/2 \text{ and } m_I = -1/2$$

Without magnetic field  $\Rightarrow$  degeneration

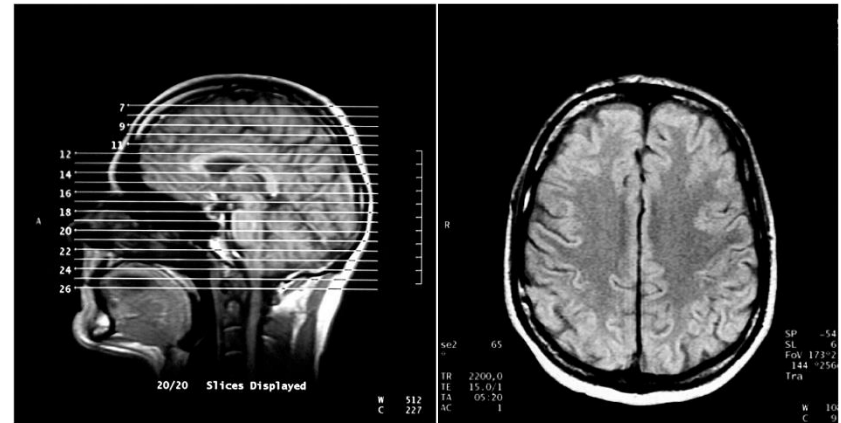
With magnetic field  $\Rightarrow$  energy difference  $\Delta E$



$$\Delta E = h\nu = \gamma \frac{h}{2\pi} B_0$$



**Nuclear spin tomography**  
(relaxation time of excited  $^1\text{H}$  nuclei)



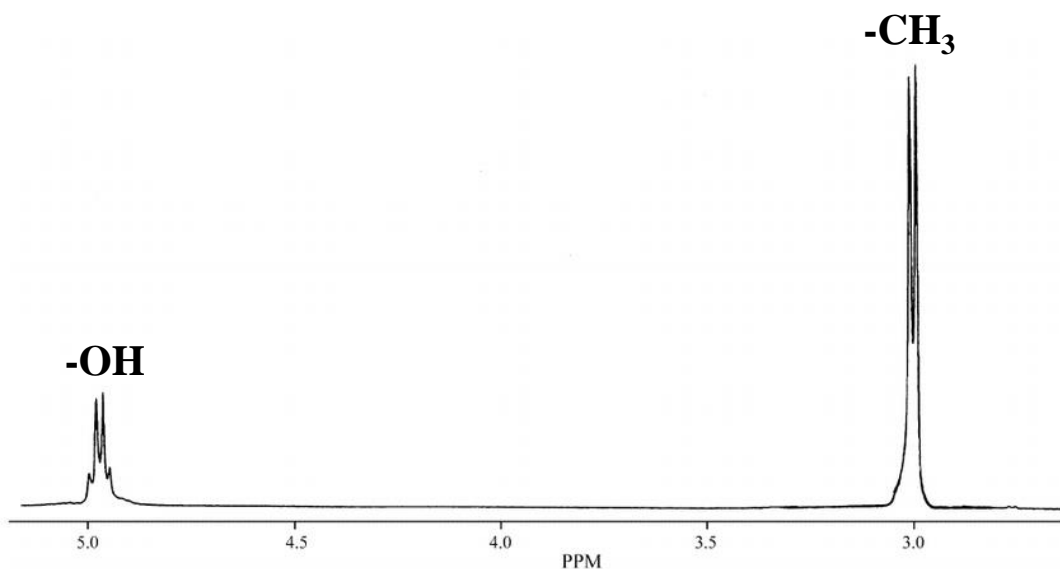
Aus "Allgemeine und Anorganische Chemie" (Binnemeyer, Jöckel, Wilker, Royner-Garham), erschienen bei Spektrum Akademischer Verlag, Heidelberg. © Walter de Gruyter GmbH. Abbildung 4.10a, pp. 144-145.

**Magnetic field strength B Resonance for  $B = 11.75$  Tesla at  $\nu = 500$  MHz (radio waves)**

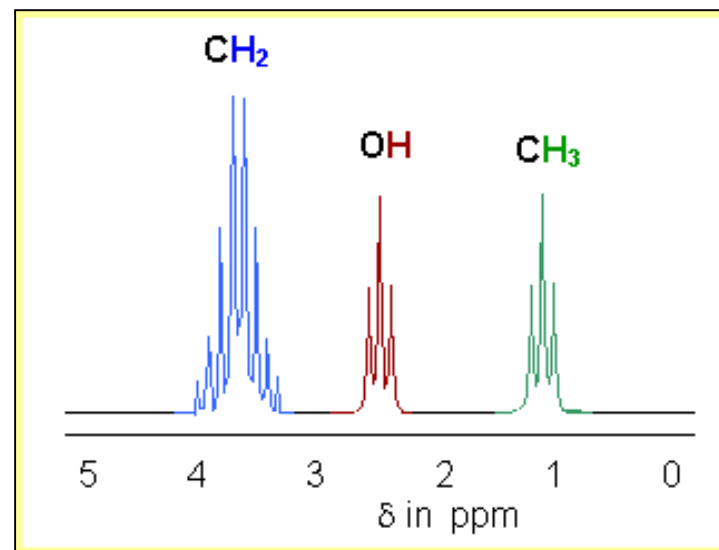
## 5.4 $^1\text{H}$ -NMR Spectroscopy

**NMR Spectroscopy (Nuclear Magnetic Resonance) is applied for the Elucidation of Molecular Structures by Monitoring the Spin  $m_I$  of Nuclei, e.g. of Protons,  $p$  ( $^1\text{H}$ )**

$^1\text{H}$ -NMR Spectrum of ethanol at 253 K



$^1\text{H}$ -NMR Spectrum of ethanol at 77 K

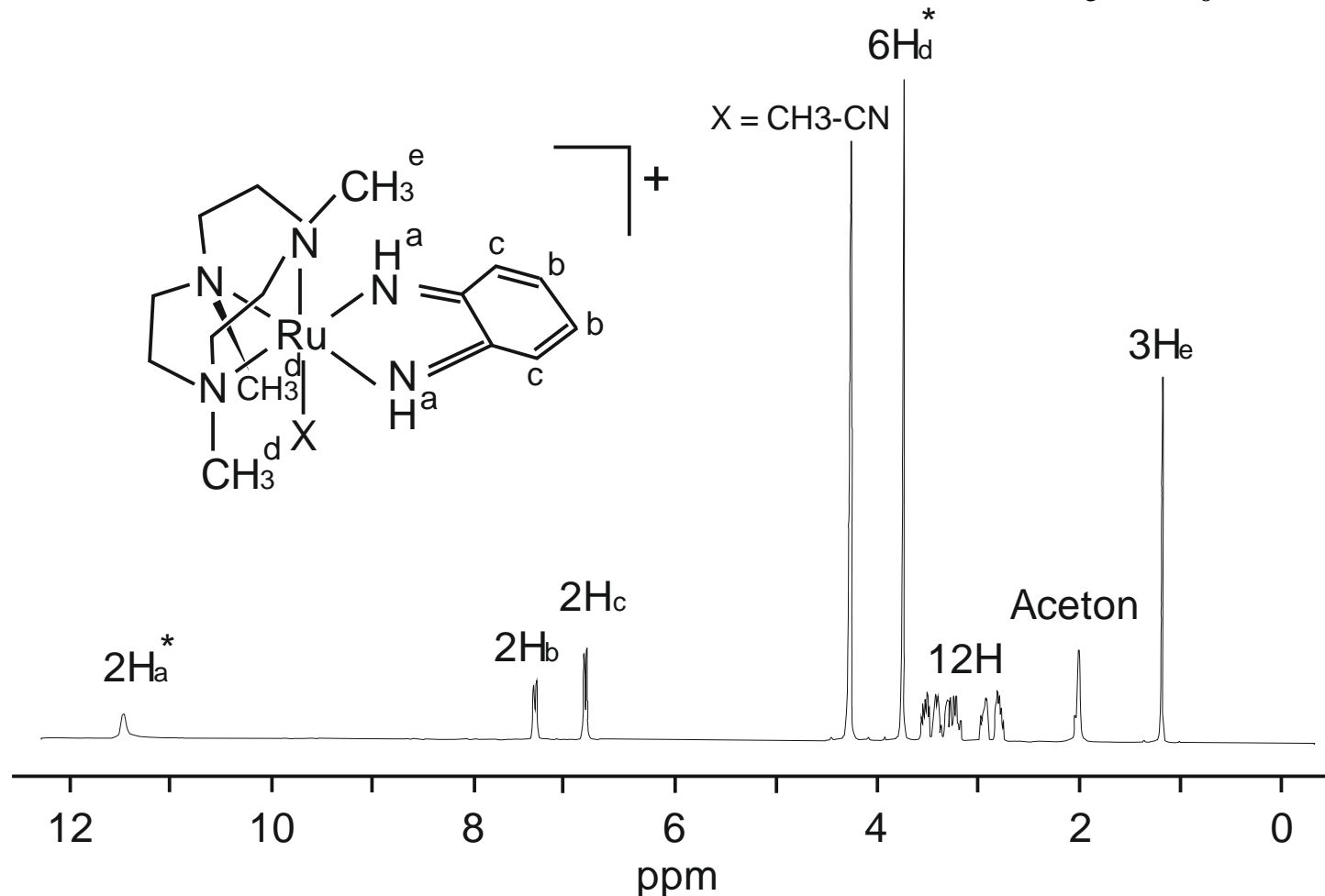


1. Each proton type yields an own NMR signal, here 2 or 3
2. NMR signals split by interaction with adjacent protons into M lines:  
 $M = (n+1)*(m+1)$  with  $n, m =$  number of adjacent protons

# 5.4 $^1\text{H}$ -NMR Spectroscopy

**NMR Spectroscopy: It can be complicated .....**

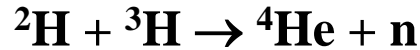
$^1\text{H}$ -NMR Spectrum of  $[(\text{tmtacn})\text{Ru}^{\text{II}}(\text{o-benzoquinonediimine})(\text{NCCH}_3)](\text{PF}_6)$  in acetone at RT



# 5.5 Hydrogen Technology

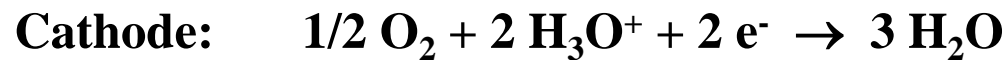
## H<sub>2</sub> is Key to the Future Energy Supply to Reduce the Combustion of Fossil Fuels

1. **Controlled nuclear fusion in magnetically trapped plasma (KFA Jülich, MPI Garching, ...)**



⇒ **Central energy generation**

2. **Combustion cells**



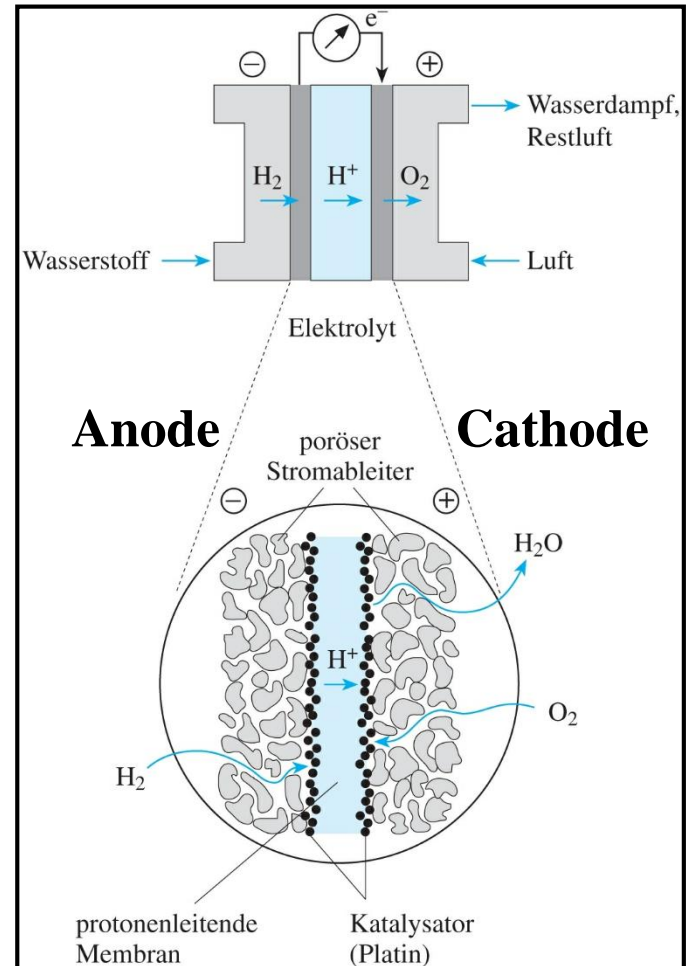
⇒ **Non-central energy generation and electric engines**

**H<sub>2</sub>-Generation:** Electrolysis (solar cells)

**H<sub>2</sub>-Transport:** Pipelines, tank ship

**H<sub>2</sub>-Storage:** Liquid reservoirs, hydrides

Simplified sketch of a fuel cell



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# 6. Noble Gases

## Contents

6.1 Occurrence and Physical Properties

6.2 Isolation

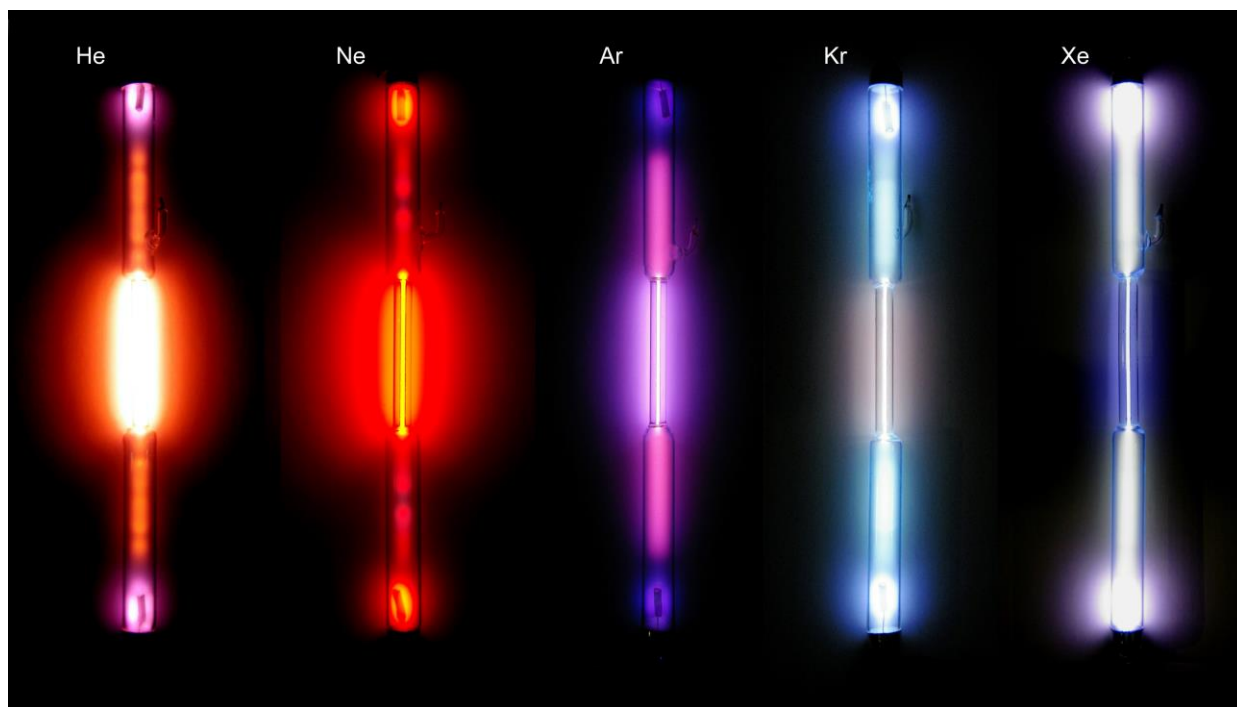
6.3 Noble Gas Compounds

6.4 VSEPR Model

6.5 Application

6.6 Gas Discharge Lamps

6.7  $^{129}\text{Xe}$ -NMR Spectroscopy



# 6.1 Occurrence and Physical Properties

**Noble Gases are inert, colour-, odour- and tasteless single Atom Gases, which occur in Stars and in the Atmosphere**

He	Helios (sun)	nuclear fusion
Ne	Neos (new)	nuclear fusion
Ar	Argos (lazy)	$^{40}\text{K} + e^-$ (K-capture) $\rightarrow$ $^{40}\text{Ar}$
Kr	Kryptos (hidden)	$^{235}\text{U} \rightarrow$ $^{90}\text{Kr} + ^{144}\text{Ba} + n$
Xe	Xenos (strange)	$^{235}\text{U} + n \rightarrow$ $^{101}\text{Zr} + ^{133}\text{Te} + 2n \rightarrow$ $^{133}\text{Xe}$
Rn	Radius (ray)	$^{226}\text{Ra} \rightarrow$ $^{222}\text{Rn} + ^4\text{He}$



Element	Electron configuration	$T_m$ [°C]	$T_b$ [°C]	IE [eV]	[kJ/mol]	Vol-% in air
He	$1s^2$	-272	-269	24.6	2370	$5 \cdot 10^{-4}$
Ne	$[\text{He}]2s^2 2p^6$	-248	-246	21.6	2080	$2 \cdot 10^{-3}$
Ar	$[\text{Ne}]3s^2 3p^6$	-189	-186	15.8	1520	<b>0.933!</b>
Kr	$[\text{Ar}]3d^{10} 4s^2 4p^6$	-157	-153	14.0	1350	$1 \cdot 10^{-4}$
Xe	$[\text{Kr}]4d^{10} 5s^2 5p^6$	-112	-108	12.1	1170	$9 \cdot 10^{-6}$
Rn	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^6$	-71	-62	10.7	1040	$6 \cdot 10^{-18}$



# 6.2 Isolation

## From Natural Gas and Air

**He:** From natural gas (up to 7 vol.-%  $\Rightarrow$  radioactive decay of U and Th in earth's crust)

**Rn:** From radioactive decay of Ra salts

**Ne, Ar, Kr, Xe:** By distillation of liquidised air (Linde process)

### Procedure

#### a. Condensation

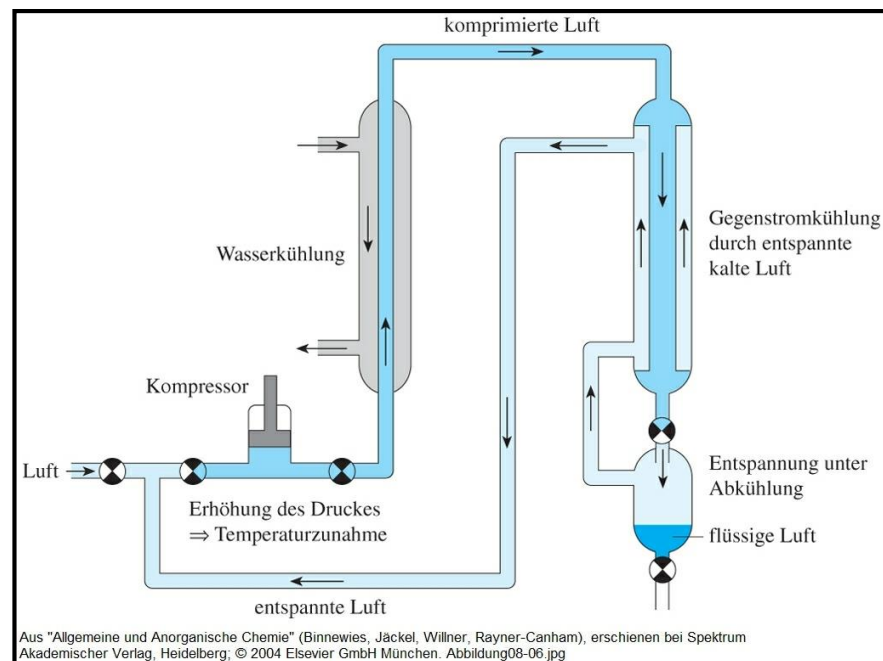
1. Fraction: He/Ne/N<sub>2</sub>

2. Fraction: N<sub>2</sub>/Ar

3. Fraction: Ar/O<sub>2</sub>

4. Fraction: O<sub>2</sub>/Kr/Xe

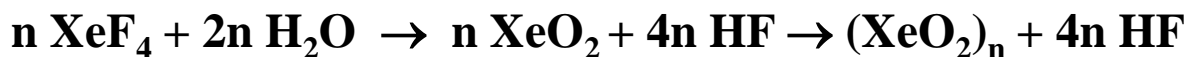
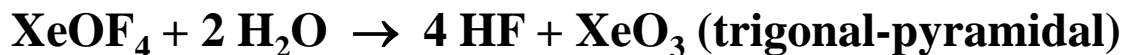
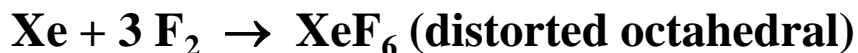
b. Removal of O<sub>2</sub> and N<sub>2</sub>  
by chemical methods



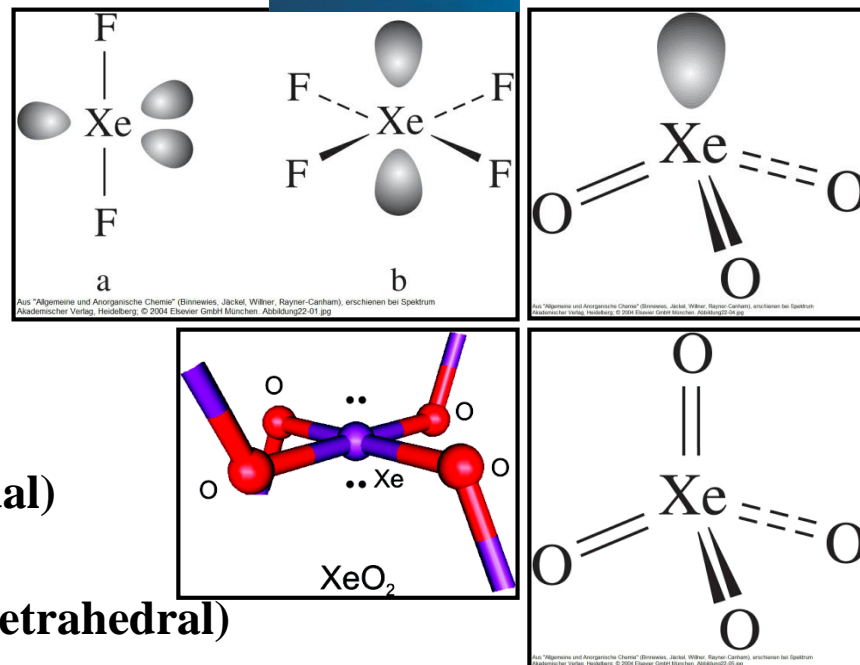
# 6.3 Noble Gas Compounds

**The Assumption that Noble Gases do not Form Compounds is not true for all Noble Gases, i.e. Kr, Xe and Rn (Neil Bartlett, Rudolf Hoppe, 1962)**

The ionisation energy of krypton and xenon is sufficiently low to enable reactions with strong oxidisers, e.g. F<sub>2</sub>



Lit.: JACS 133 (2011) 6265-6269



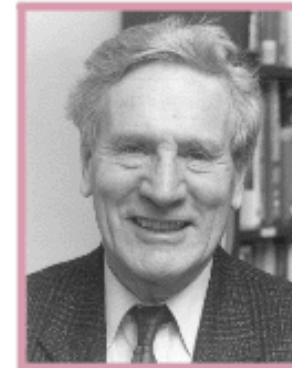


## 6.4 VSEPR Model

**Valence Shell Electron Pair Repulsion Model is based on the Fact that Electron Pairs reject themselves and thus try to arrange the largest possible Distance between them**

### History

**Ronald Gillespie and Ronald Nyholm published this theory, by which the structure of simple molecules of the type  $AB_n$  can be predicted.**



**Ronald Gillespie**

### Basics

**The Lewis model of valence electron pairs, in which two valence electrons having antiparallel spin are combined to form a valence electron pair, which can connect atoms.**

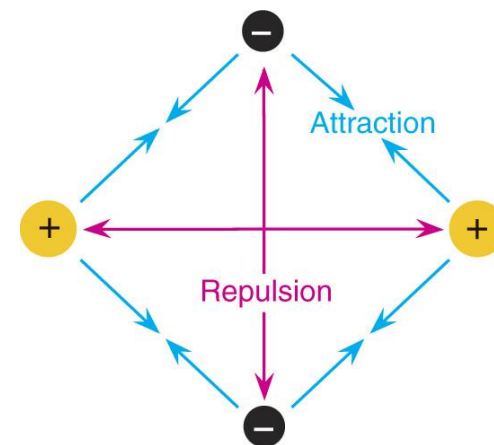
### Thesis

**The 3D structure of molecules are determined by repelling forces between the electron pairs of the valence shell.**

# 6.4 VSEPR Model

## Physical Basis: Electromagnetism as the fundamental Interaction

- Some charges/poles repel each other (+ and + or - and -)
- Opposite charges/poles attract each other (+ and -)



**Electrons** as well as the **atomic shell** are negatively charged

⇒ Inner electrons are spherical distributed

⇒ Valence electrons (bond and non-bond) arrange in a way, that the repellent interactions between them are minimised

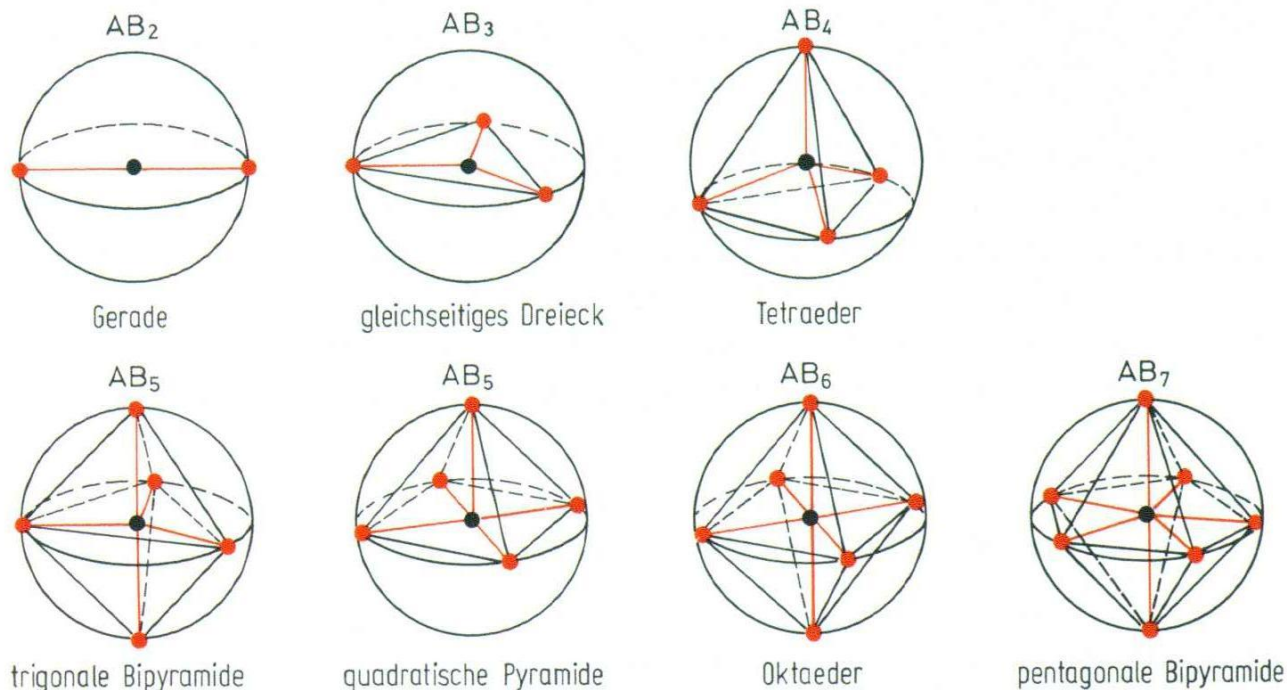
⇒ The structure of molecules is mostly determined by the electromagnetic interaction between the valence electrons

**Molecule structure = Connectivity of atoms + 3D arrangement in space**

# 6.4 VSEPR Model

## VSEPR Model can be reduced to four Rules for the Structure Prediction

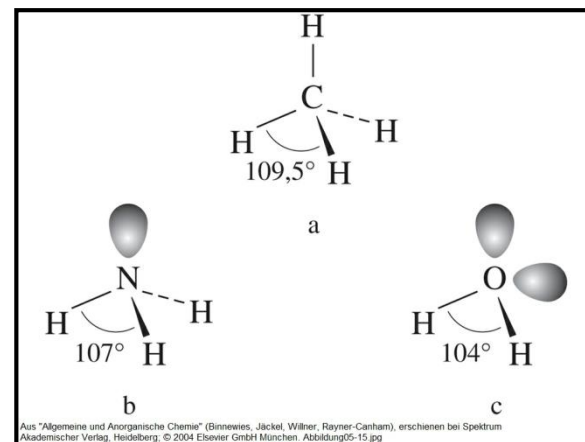
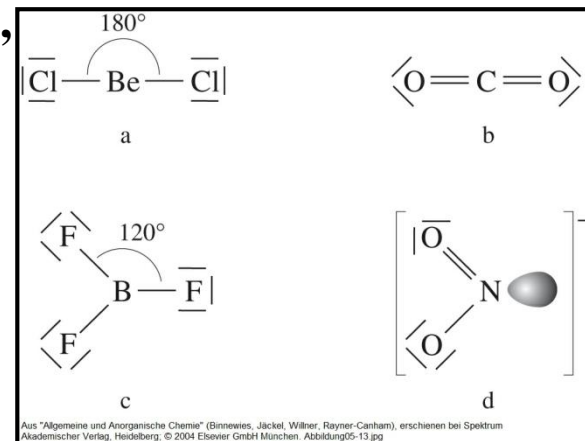
**1<sup>st</sup> Rule:** In molecules of type  $AB_n$  the bonding and non-bonding electron pairs arrange themselves in the valence shell of the central atom A in such a way that their distance becomes maximum. Bonding  $\pi$ -electron pairs are not taken into account separately, i.e. double and triple bonds are regarded as a single domain.



Lit.: E. Riedel, Anorganische Chemie  
Walter de Gruyter 2004, 136f

# 6.4 VSEPR Model

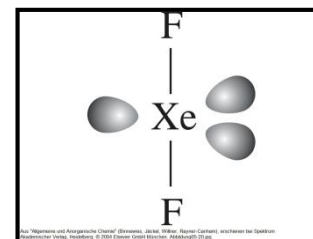
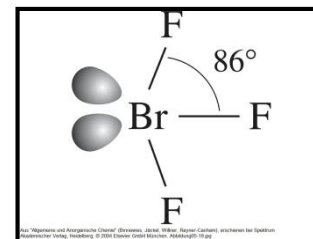
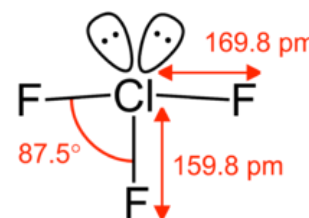
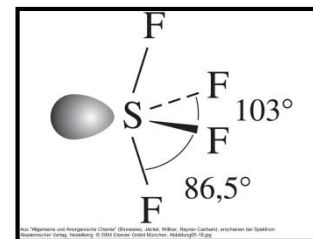
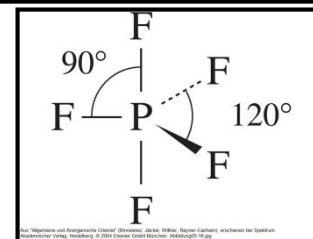
Number of VEPs	Molecule type	Arrangement of atoms	Examples
2	AB <sub>2</sub>	linear	BeCl <sub>2</sub> , CO <sub>2</sub> , NO <sub>2</sub> <sup>+</sup> , ZnCl <sub>2</sub> , HgCl <sub>2</sub>
3	AB <sub>3</sub>	trigonal-planar	BF <sub>3</sub> , BCl <sub>3</sub> , SO <sub>3</sub>
	AB <sub>2</sub> E	bent	NO <sub>2</sub> <sup>-</sup> , SnCl <sub>2</sub> , O <sub>3</sub>
4	AB <sub>4</sub>	tetrahedral	CH <sub>4</sub> , XeO <sub>4</sub>
	AB <sub>3</sub> E	trig.-pyramidal	NH <sub>3</sub> , XeO <sub>3</sub>
	AB <sub>2</sub> E <sub>2</sub>	bent	H <sub>2</sub> O, XeO <sub>2</sub> *



Lit.: \*JACS 133 (2011) 6265

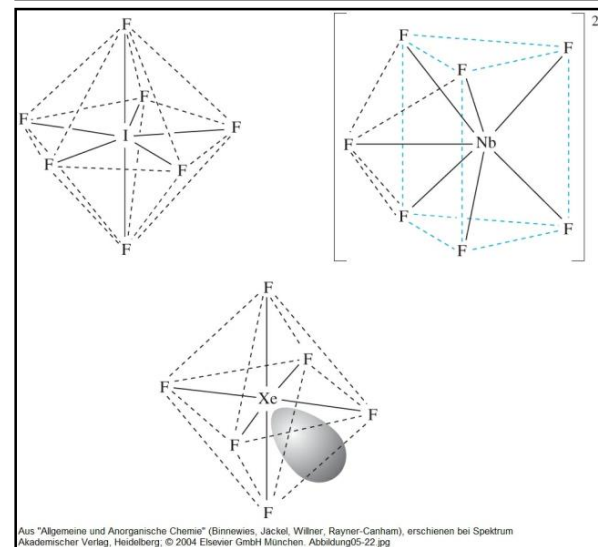
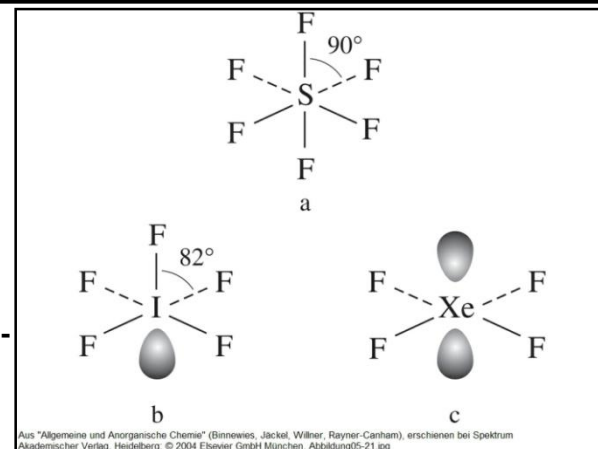
# 6.4 VSEPR Model

Number of VEPs	Molecule type	Arrangement of atoms	Examples
5	$AB_5$	trigonal-bipyramidal	$PF_5$ , $PCl_5$
	$AB_4E$	rocker-shaped	$SF_4$ , $SeF_4$ , $SCl_4$
	$AB_3E_2$	T-shaped	$BrF_3$ , $ClF_3$
	$AB_2E_3$	linear	$KrF_2$ , $XeF_2$ , $I_3^-$ , $ICl_2^-$



# 6.4 VSEPR Model

Number of VEPs	Molecule type	Arrangement of atoms	Examples
6	$AB_6$	octahedral	$SF_6$ , $SeF_6$ , $PF_6^-$
	$AB_5E$	square-pyramidal	$ClF_5$ , $BrF_5$ , $IF_5$
	$AB_4E_2$	square-planar	$XeF_4$ , $BrF_4^-$ , $ICl_4^-$
7	$AB_7$	pentagonal-bipyramidal	$IF_7$
	$AB_6E$	distorted octahedral	$XeF_6$
		capped trigonal-prismatic	$[NbF_7]^{2-}$



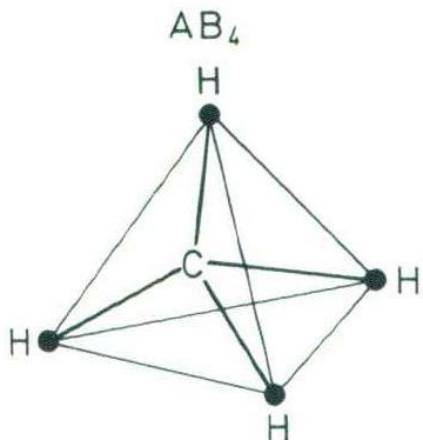
## 6.4 VSEPR Model

**2<sup>nd</sup> Rule:** The lone pairs of electrons E are located in a molecule of type  $AB_nE_m$  only in the field of an atomic nucleus and therefore take up more space than that bonding electron pairs. Therefore, they reduce the bond angle in a rocker-like manner.

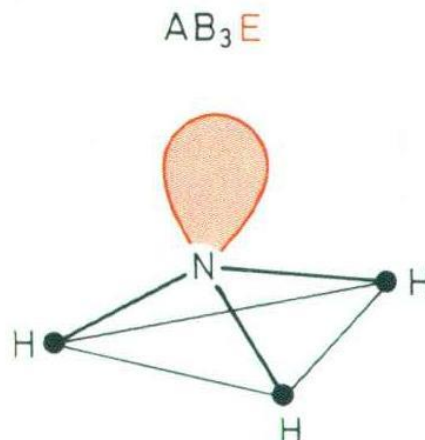
**Example:** Tetrahedral structures  $AB_{4-x}E_x$  ( $x = 0 - 2$ )

Lit.: E. Riedel, Anorganische Chemie  
Walter de Gruyter 2004, 136f

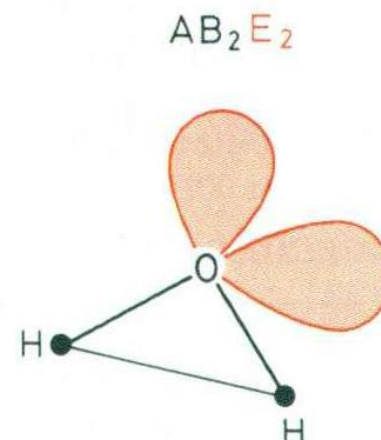
Beispiele für die tetraedrischen Strukturen  $AB_4$ ,  $AB_3E$  und  $AB_2E_2$  sind  $CH_4$ ,  $NH_3$  und  $H_2O$



**Bond angle:**  $109,5^\circ$



$107^\circ$

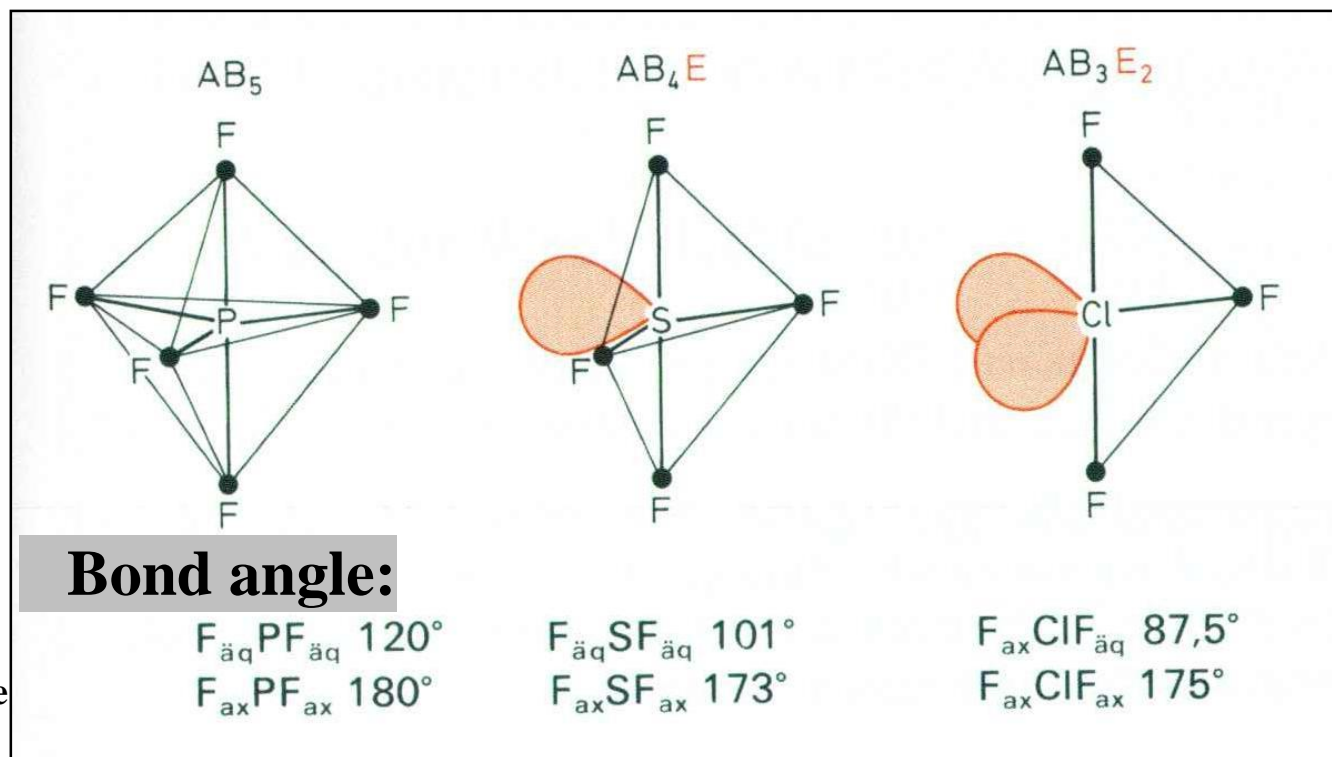


$104,5^\circ$

# 6.4 VSEPR Model

**2<sup>nd</sup> Rule:** The lone pairs of electrons E are located in a molecule of type  $AB_nE_m$  only in the field of an atomic nucleus and therefore take up more space than that bonding electron pairs. Thus, they reduce the bond angle in a rocker-like manner.

**Example:** Pentagonal-bipyramidal structures  $AB_{5-x}E_x$  ( $x = 0 - 2$ )



Lit.: E. Riedel, Anorganische Chemie  
Walter de Gruyter 2004, 136f

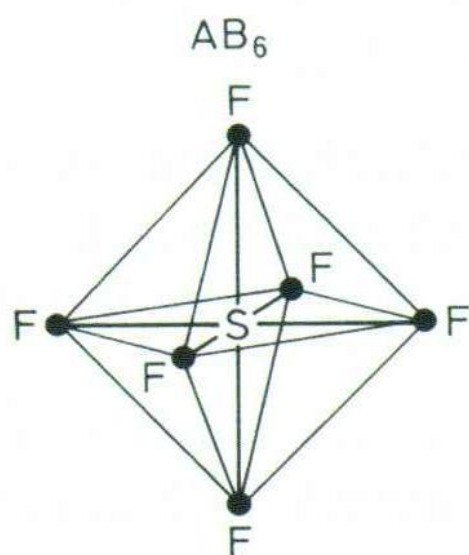


## 6.4 VSEPR Model

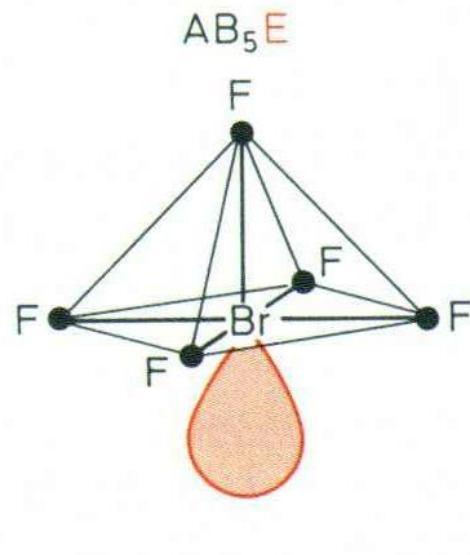
**2<sup>nd</sup> Rule:** The lone pairs of electrons E are located in a molecule of type  $AB_nE_m$  only in the field of an atomic nucleus and therefore take up more space than that bonding electron pairs. Thus, they reduce the bond angle in a rocker-like manner.

**Example:** Octahedral structures  $AB_{6-x}E_x$  ( $x = 0 - 2$ )

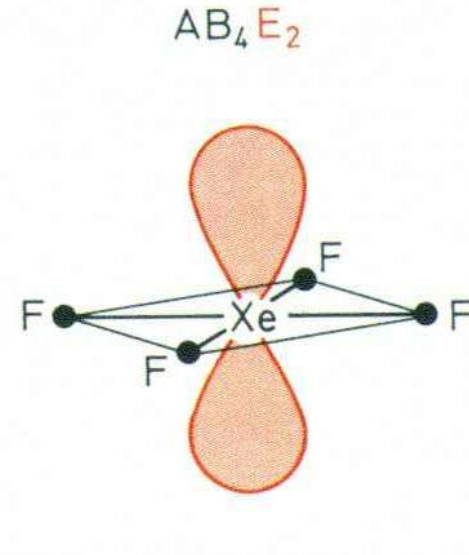
Lit.: E. Riedel, Anorganische Chemie  
Walter de Gruyter 2004, 136f



**Bond angle:** FSF 90°



$F_{ax}BrF$  85°



FXeF 90°

## 6.4 VSEPR Model

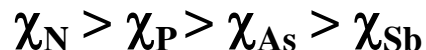
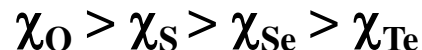
**3<sup>rd</sup> Rule:** The repulsive force of an AB bond decreases as the difference in electronegativity (EN)  $\chi$  between A and B increases. The valence angles therefore decrease as the EN difference increases.

a) **Electronegativity of the central atom A**

<u>H<sub>2</sub>A</u>	Bond angle [°]	<u>AF<sub>3</sub></u>	Bond angle [°]
H <sub>2</sub> O	104.5	NF <sub>3</sub>	102.4
H <sub>2</sub> S	92.3	PF <sub>3</sub>	97.4
H <sub>2</sub> Se	91.0	AsF <sub>3</sub>	96.0
H <sub>2</sub> Te	89.5	SbF <sub>3</sub>	95.0

### Causes

- **Trend of the EN values**



- **Increasing energy difference between the ns- and np-orbitals of the central atoms reduces extent of hybridisation**

## 6.4 VSEPR Model

**3<sup>rd</sup> Rule:** The repulsive force of an AB bond decreases as the difference in electronegativity (EN)  $\chi$  between A and B increases. The valence angles therefore decrease as the EN difference increases.

### b) Electronegativity of the ligands B

<u>PB<sub>3</sub></u>	Bond angle [°]	<u>AsB<sub>3</sub></u>	Bond angle [°]
PF <sub>3</sub>	97.4	AsF <sub>3</sub>	96.0
PCl <sub>3</sub>	100.1	AsCl <sub>3</sub>	98.6
PBr <sub>3</sub>	101.0	AsBr <sub>3</sub>	99.7
PI <sub>3</sub>	102.0	AsI <sub>3</sub>	100.2

### Causes

- Trend of the EN values  
 $\chi_{\text{F}} > \chi_{\text{Cl}} > \chi_{\text{Br}} > \chi_{\text{I}}$
- Increasing energy difference between the ns- and np-orbitals of the central atoms reduces extent of hybridisation

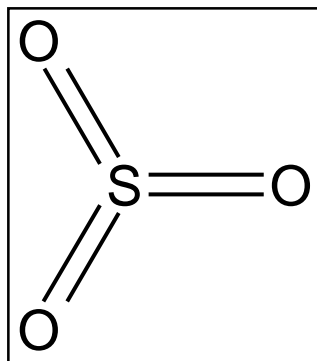
# 6.4 VSEPR Model

**4<sup>th</sup> Rule: Multiple bonds are formally treated like single bonds**

## Trigonal-planar structure

**BF<sub>3</sub>     3 Single bonds**

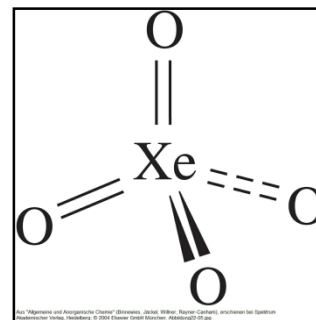
**SO<sub>3</sub>     3 Double bonds**



## Tetrahedral structure

**CH<sub>4</sub>     4 Single bonds**

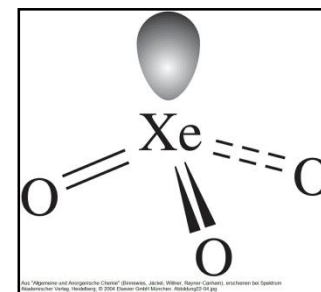
**XeO<sub>4</sub>     4 Double bonds**



## Trigonal-pyramidal structure

**NH<sub>3</sub>     3 Single bonds + 1 lone electron pair**

**XeO<sub>3</sub>     3 Double bonds + 1 lone electron pair**



## 6.4 VSEPR Model

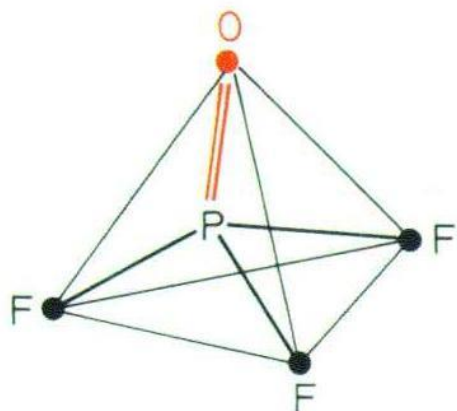
**4<sup>th</sup> Rule:** Multiple bonds are formally treated like single bonds.

However, multiple bonds require more space and thus reduce the bond angle

Phosphate  $\text{PO}_4^{3-}$



Phosphorylfluoride  $\text{POF}_3$

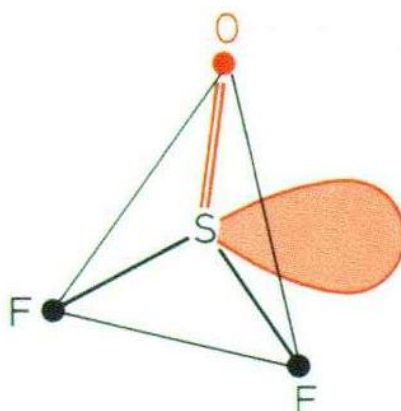


**Bond angle:** FPF  $101^\circ$

Sulphite  $\text{SO}_3^{2-}$



Thionylfluoride  $\text{SOF}_2$

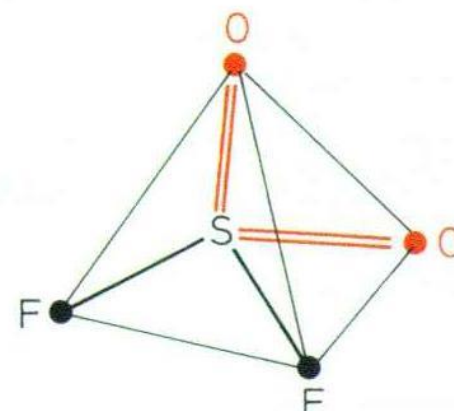


OSF  $107^\circ$   
FSF  $93^\circ$

Sulphate  $\text{SO}_4^{2-}$



Sulfurylfluoride  $\text{SO}_2\text{F}_2$

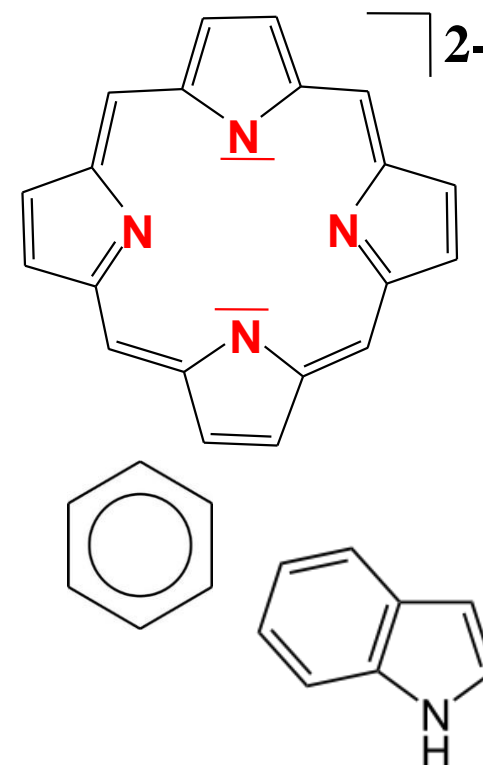
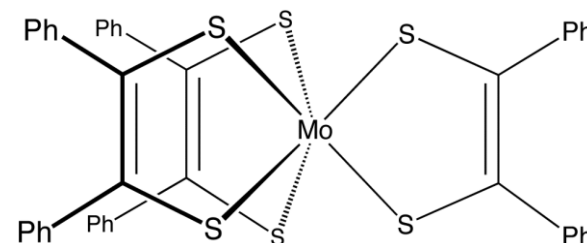


OSO  $124^\circ$   
FSF  $96^\circ$

# 6.4 VSEPR Model

## Limits of the Theory

- a) **Transition metal compounds (complexes), e.g.  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{PtCl}_4]^{2-}$  are square-planar**  
→ **Ligand field theory**
- b) **Liganden, which enforces structure for sterical reasons**  
**Chelating ligands:  $[\text{M}(\text{S}_2\text{C}_2(\text{Ph})_2)_3]$  with  $\text{M} = \text{Re}, \text{Mo}$  are trigonal-prismatic**  
**Macrocyclic ligands: Porphyrin enforces square-planar arrangement**
- c) **For molecules with delocalized electrons, especially aromatics such as benzene or 3,4-benzopyrrole, no statement can be made about the spatial structure, since the interactions between the atoms involved have a strong impact on the spatial structure of these molecules**  
→ **Molecule orbital (MO) theory**



# 6.4 VSEPR Model

## Summary

- The VSEPR theory is an empirical model based on observations. It only allows to roughly estimate the molecular structure of small molecules. However, a proper calculation of the structure is not possible.
- The model is solely accurate for elements of the first two periods. Once d-orbitals are present, deviations from predictions of the VSEPR model may be observed.
- The model is not suitable for sterically demanding ligands, molecules with delocalized electrons or some transition metal compounds.
- In order to make accurate predictions about the construction of more complex molecules, one must apply advanced models → Ligand field (LF) & MO theory

Steric No.	VSEPR Geometries				
	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal Planar	 Bent or Angular			
4	 Tetrahedral	 Trigonal Pyramid	 Bent or Angular		
5	 Trigonal Bipyramid	 Sawhorse or Seesaw	 T-shape	 Linear	
6	 Octahedral	 Square Pyramid	 Square Planar	 T-shape	 Linear

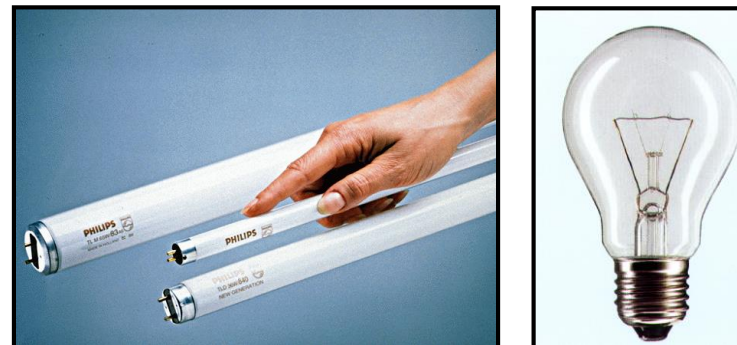
# 6.5 Technical Application

**In Light Sources, Excimer LASER, Balloons, as Respiratory Gas, as Inert Gas, etc.**

## 1. Light sources

Ar, Kr, Xe in incandescent lamps

Ar, Ne, Kr, Xe in gas discharge lamps

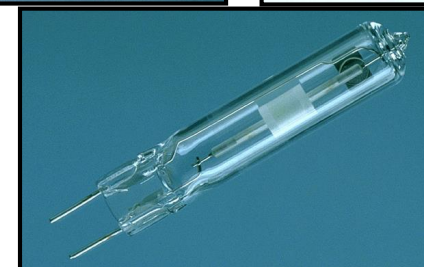


## 2. Excimer LASER and plasma displays

$\text{Ar}_2^* \rightarrow 2 \text{Ar} + h\nu$  (126 nm)

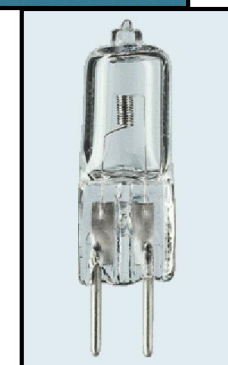
$\text{Kr}_2^* \rightarrow 2 \text{Kr} + h\nu$  (146 nm)

$\text{Xe}_2^* \rightarrow 2 \text{Xe} + h\nu$  (172 nm)



## 3. Filling of balloons

Low density of He ~ 0.1785 g/l



## 4. Respiratory gas

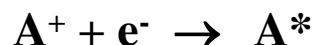
He-O<sub>2</sub> for deep divers (He dissolves less in blood than N<sub>2</sub>)



# 6.6 Gas Discharge Lamps

**Light Generation is based on the Light Emission of excited Atoms, e.g. Hg, Na, or Noble Gases from the Gas Phase**

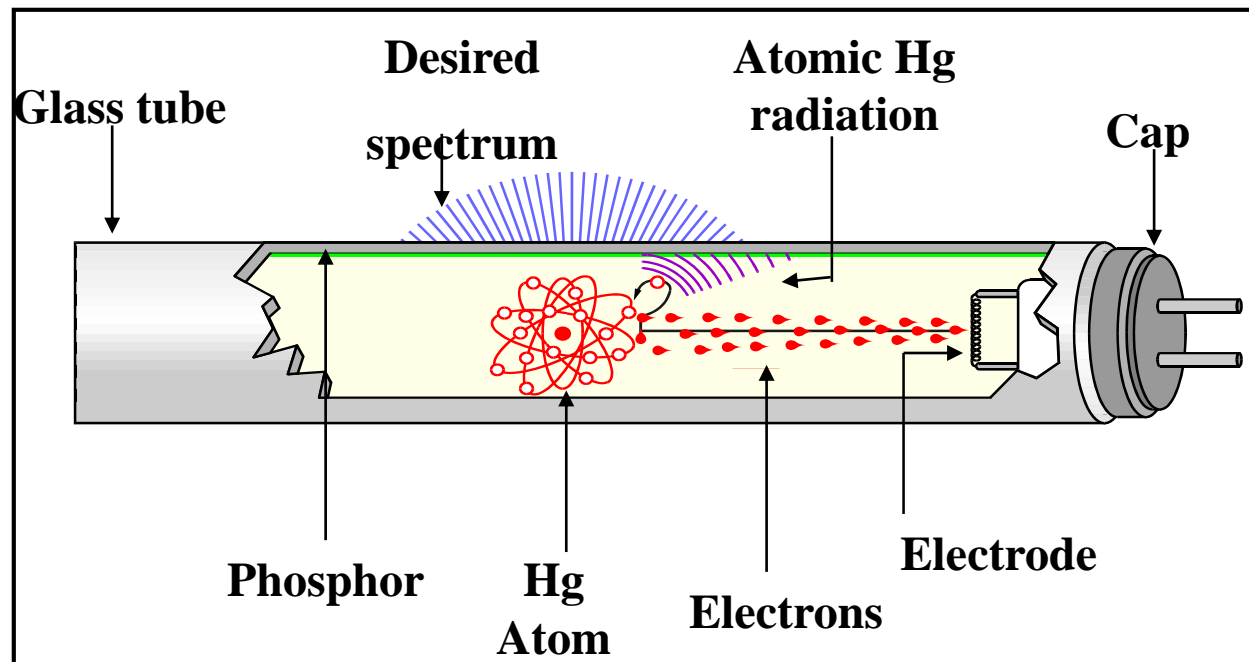
## Principle of light generation



## Fluorescent lamps

comprise 3 - 5 mg liquid Hg, that goes into the gas phase during lamp operation

Phosphors: Inorganic solid-state compounds  $\Rightarrow$  Oxides, sulphides, nitrides, (halides)



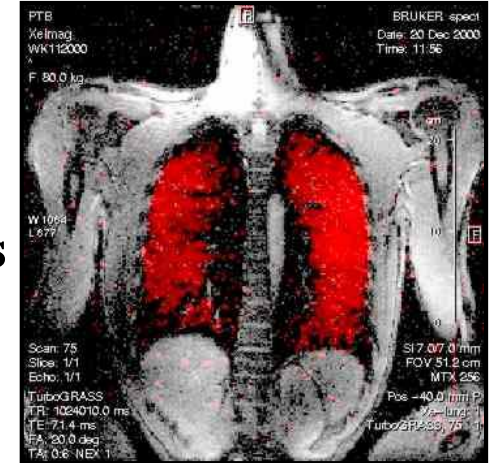
# 6.7 $^{129}\text{Xe}$ -NMR Spectroscopy

## Application in Chemistry and Medicine

### Medicine

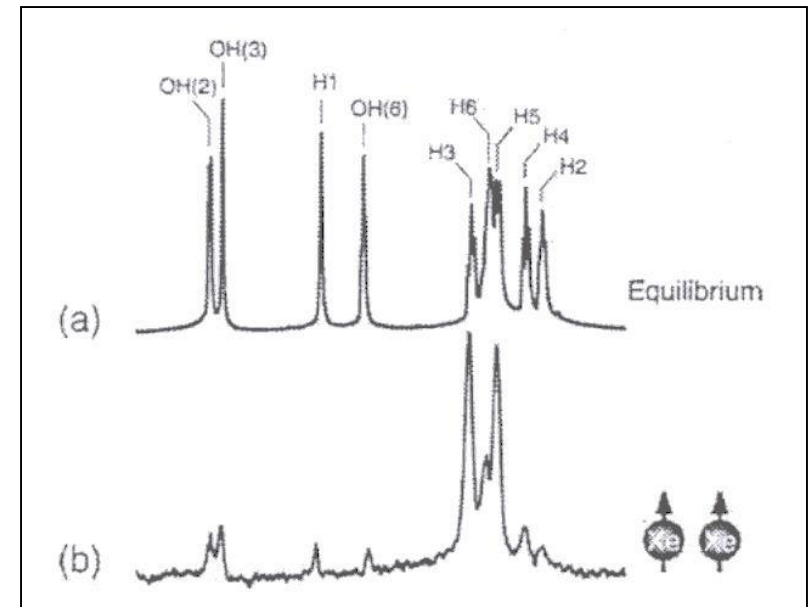
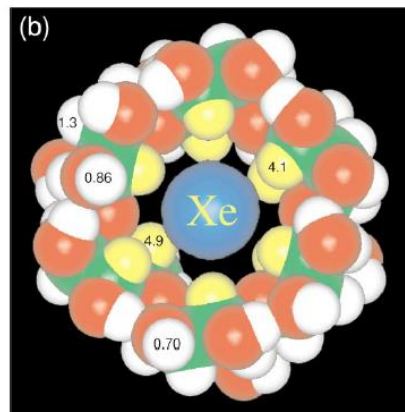
Contrast enhancement in nuclear spin tomography diagnostics

⇒ Improved imaging of vessels, inner organs, body cavities, e.g. lung



### Chemistry

Structure elucidation of complex molecules



# 7. Oxygen

## Outline

**7.1 Occurrence in Earth's Atmosphere**

**7.2 Isolation and Reactivity**

**7.3 Physical Properties**

**7.4 Atmosphere Chemistry**

**7.5 Oxygen Compounds**

**7.6 Technical Application**

# 7.1 Occurrence in Earth's Atmosphere

**The Presence of Oxygen (O<sub>2</sub> and O<sub>3</sub>) in Earth's Atmosphere is the Result of Biological Activity → Photosynthesis:**  $6 \text{CO}_2 + 6 \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2$

## Average composition of dry air

N <sub>2</sub>	78.08%
O <sub>2</sub>	20.95%
Ar	0.93%
CO <sub>2</sub>	0.043%
Ne	0.0018%
CH <sub>4</sub> , Kr, N <sub>2</sub> O, H <sub>2</sub> , CO, Xe,	< 0.001%
SF <sub>6</sub> , NF <sub>3</sub> , CF <sub>4</sub> , He, .....	(< 10 ppm)

## Oxygen isotopes

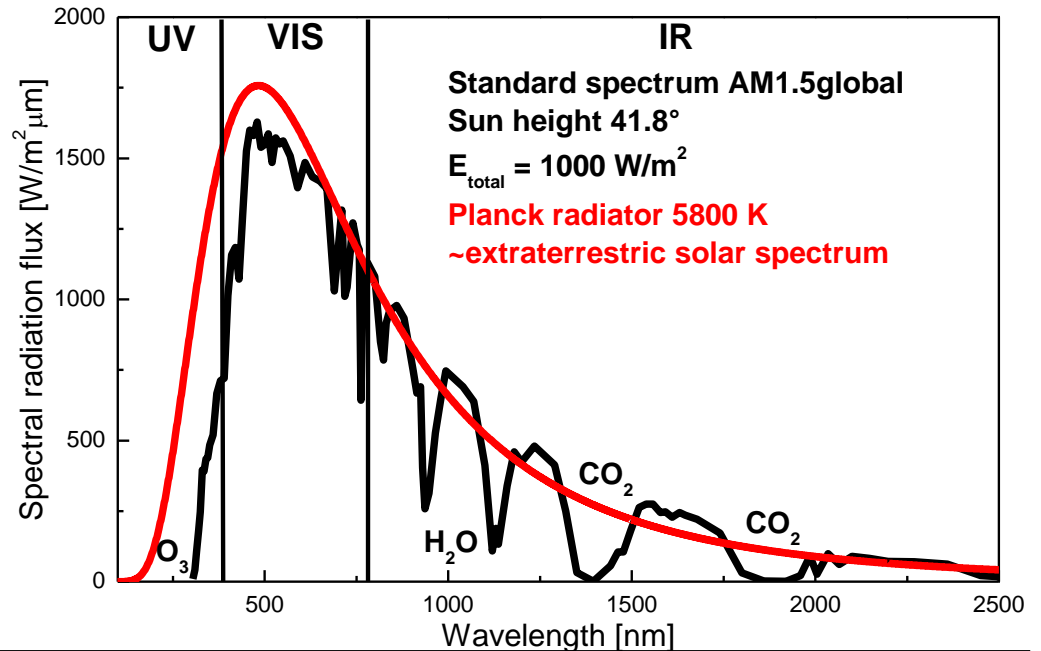
<sup>16</sup> O	99.762%
<sup>17</sup> O	0.038%
<sup>18</sup> O	0.200%

## Geology, climatology, palaeontology

H<sub>2</sub><sup>18</sup>O enriches in the oceans due to evaporation

⇒ T-Sensor: Incorporation of <sup>18</sup>O in foraminifers, molluscs, and lime

⇒ Mass spectroscopic determination

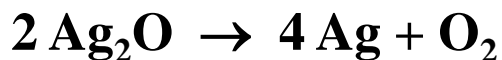
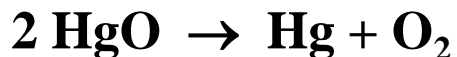


# 7.2 Synthesis and Reactivity

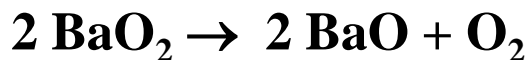
## Synthesis

### Molecular Oxygen O<sub>2</sub>

a) Heating of noble metal oxides

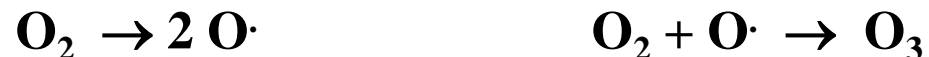


b) Decomposition of peroxides



### Ozone O<sub>3</sub>

a) Photolysis of O<sub>2</sub> or sparks in O<sub>2</sub>



(Discharges, ozone layer: stratosphere)

b) Photolysis of NO<sub>2</sub> in air



(Summer smog: troposphere)

## Reactivity

- Molecular Oxygen is rather stable and inert and ambient T:  $\Delta H_{\text{diss}} = 498 \text{ kJ/mol}$
- Ozone is thermodynamically instable and decomposes upon heating or in the presence of catalysts such as MnO<sub>2</sub> or PbO<sub>2</sub> according to  $2 \text{O}_3 \rightarrow 3 \text{O}_2$
- O<sub>2</sub> and O<sub>3</sub> are strong oxidisers  
 $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$  and  $\text{S} + \text{O}_3 \rightarrow \text{SO}_3$

# 7.3 Physical Properties

**Molecular Oxygen and Ozone are highly soluble in Water  
(Much better than Carbohydrates)**

## Solubility of $O_2$ in $H_2O$

- at 25 °C and 1 bar ~ 40 mg per litre
- Air contains almost 21%  $O_2 \Rightarrow \sim 8$  mg per litre
- Solubility decreases with increasing temperature  
 $\Rightarrow$  Cold waters are full of fish (Humboldt stream)
- Oxygen free chemistry in solution requires thorough flushing by an inert gas (e.g. Ar or  $N_2$ )



## Toxicity of $O_2$ and $O_3$

< 8%  $O_2 \Rightarrow$  blanket by Oxygen deficiency

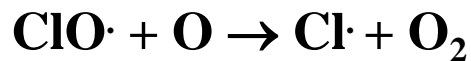
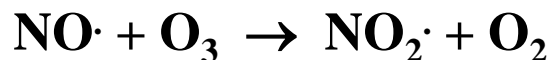
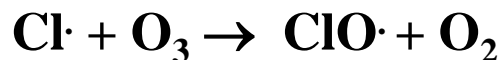
> 60%  $O_2 \Rightarrow$  Formation of harmful hyperoxide  $O_2^-$

$O_3$  is extremely toxic: MAK-value = 0.2 mg/cm<sup>3</sup> ~ 0.1 ppm (parts per million)

# 7.4 Atmosphere Chemistry

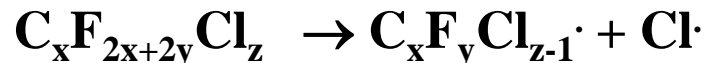
**By Formation of O<sub>2</sub> the Ozone Layer was build-up about 500 – 600 Mill. Years ago**

Stratosphere (15 - 50 km)

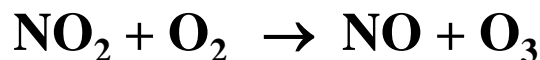
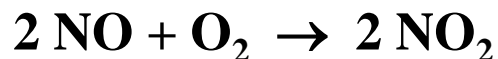


Cl· stems from CFC = chlorofluorocarbon

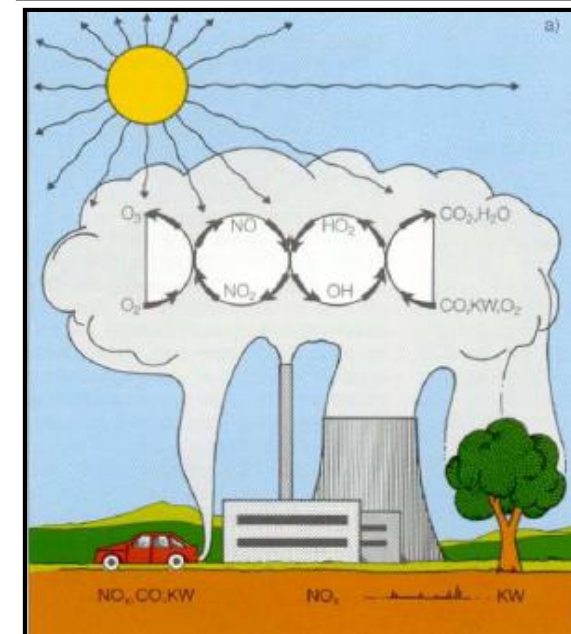
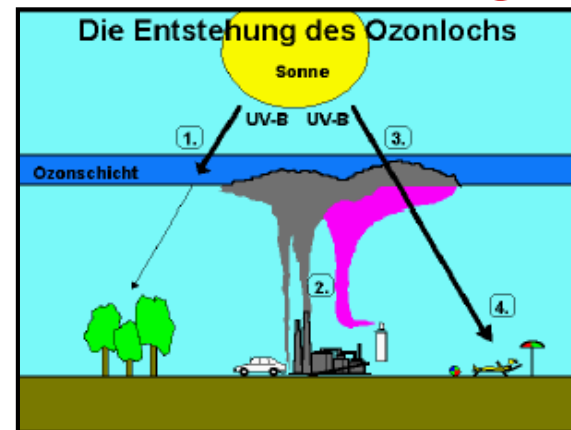
e.g. CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub>



Troposphere (0 – 10 km)



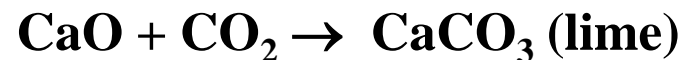
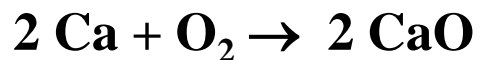
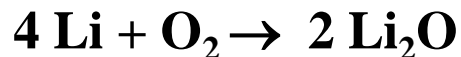
(Summer smog: O<sub>3</sub> > 180 µg/m<sup>3</sup> air)



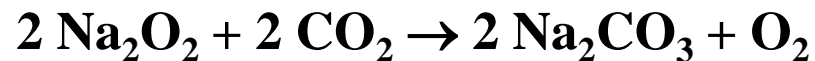
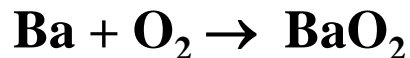
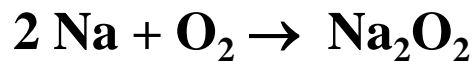
# 7.5 Oxygen Compounds

## Oxygen Forms Oxides, Peroxides, Hyperoxides, and Ozonides

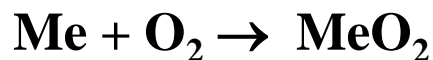
### Oxides $O^{2-}$ (-2)



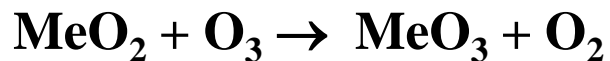
### Peroxides $O_2^{2-}$ (-1)



### Hyperoxides $O_2^-$ (-1/2)



### Ozonides $O_3^-$ (-1/3)

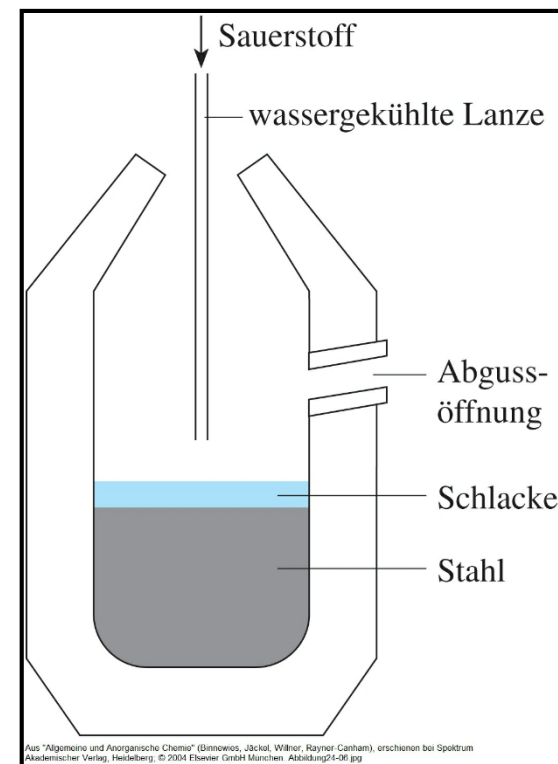




# 7.6 Technical Application

## Molecular Oxygen (O<sub>2</sub>)

- **Steel production**  
(Reduction of the carbon content:  $2\text{ C} + \text{O}_2 \rightarrow 2\text{ CO}$ )
- **Welding (acetylene / O<sub>2</sub>)**
- **Waste water treatment**
- **Drinking water treatment**
- **Respiratory gas (blended with N<sub>2</sub> or He)**
- **Medicine (Oxygen treatment)**



## Ozone (O<sub>3</sub>)

- **Surfae, water, and air treatment (killing of microorganisms)**
- **Organic chemistry (ozonolysis)**

