Water Treatment with (Photo) Chemical Methods

Contents

Science is searching for a perpetual motion machine. It has found it: It is itself. (Victor Hugo)

Literature

Chemistry

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- C.E. Mortimer, U. Müller, Chemie, Thieme, 8. Auflage 2003
- M. Binnewies, M. Jäckel, H. Willner, G. Rayner-Canham, Allgemeine und Anorganische Chemie, Spektrum, 1. Auflage 2004
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Water

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Photochemistry

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- T. Oppenländer, Photochemical Purification of Water and Air, Wiley-VCH 2003

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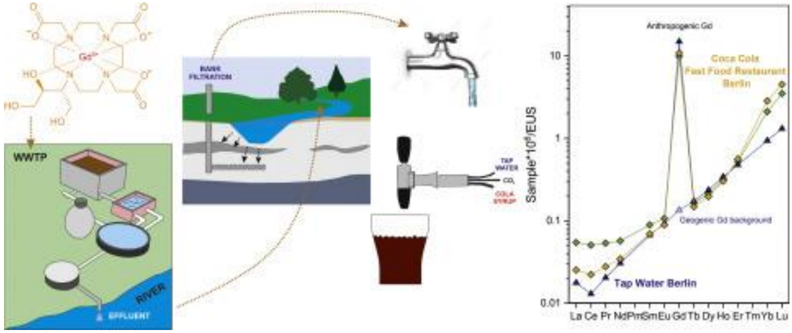
- **Rethinking wastewater risks and monitoring in light of the COVID-19 pandemic, Nature Sustainability 3 (2020) 981**
- **First environmental surveillance for the presence of SARS-CoV-2 RNA in wastewater and river water in Japan, Science of the Total Environment 737 (2020) 140405**
- **First detection of SARS-CoV-2 RNA in wastewater in North America: A study in Louisiana, USA, Science of the Total Environment 743 (2020) 140621**
- **Presence and infectivity of SARS-CoV-2 virus in wastewaters and rivers, Science of the Total Environment 744 (2020) 140911**
- **First proof of the capability of wastewater surveillance for COVID-19 in India through detection of genetic material of SARS-CoV-2, Science of the Total Environment 746 (2020) 141326**
- **Coronaviruses in wastewater processes: Source, fate and potential risks, Environment International 143 (2020) 105962**

Media

Recent Press Releases (Selection)



- **Legionella alarm: tenants are increasingly worried**
  https://www.wassertest-online.de/blog/legionellen/

- **Drug residues in cola from McDonald's and Burger King**
  http://www.shortnews.de/id/1089077/medikamentenrueckstaende-in-cola-von-mcdonald-s-und-burger-king

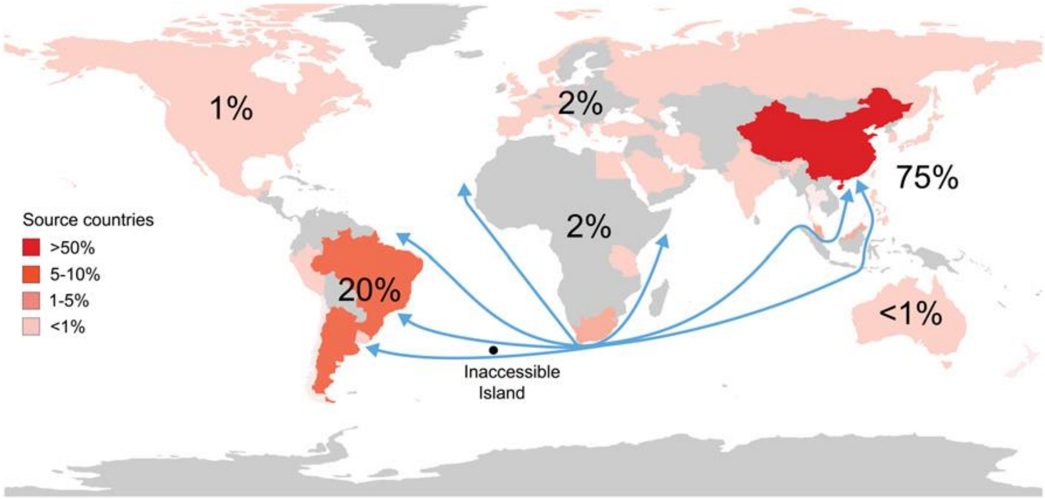
- **Multi-resistant germs in surface waters**
  http://www.tagesschau.de/multimedia/video/video-374579.html

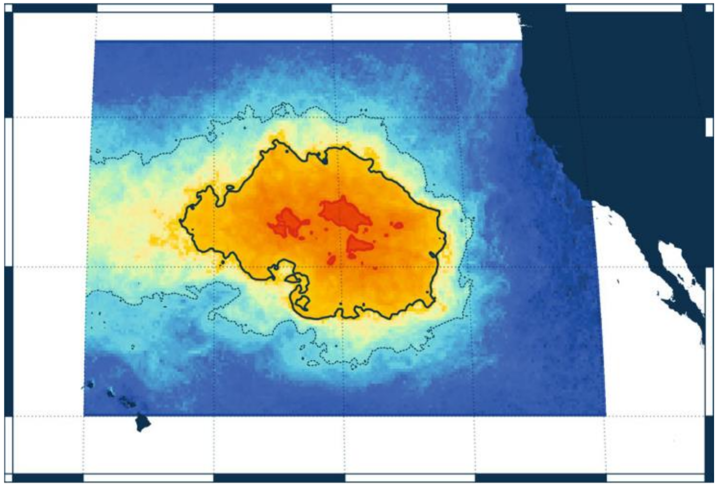
- **More plastic than fish in the sea**
  http://www.sueddeutsche.de/wissen/kunststoff-im-ozean-mehr-plastik-als-fische-im-meer-1.2826984

- **New study: tap water worldwide contains plastic**
  https://utopia.de/leitungswasser-plastik-mikroplastik-63184/

Media

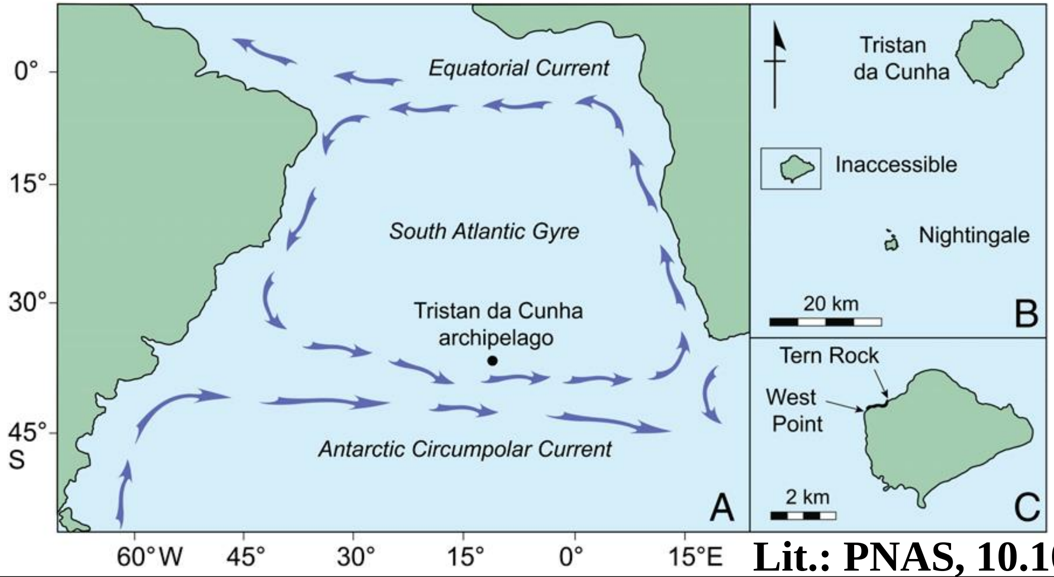
Scientific Literature (Selection)





Lit.: Scientific Reports 8 (2018) 4666

Source: BBC



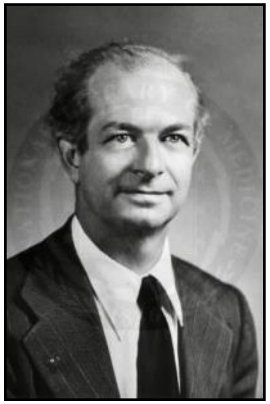
Lit.: PNAS, 10.1073/pnas.1909816116

1. Introduction

What is Chemistry?

“Chemistry is the study of substances, their structure, their properties and the reactions that create other substances from them“

(Linus Carl Pauling 1956, Nobel Prizes: Chemistry 1954, Peace 1962)

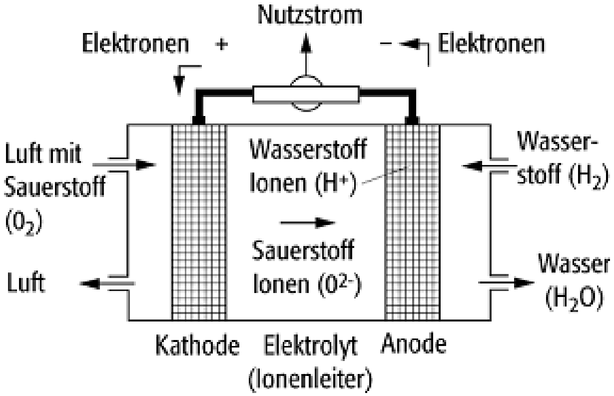


Example

$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g)$ **Chemical process (e.g. redox reaction)**

$\downarrow$

$2\ H_2O(s)$ **Physical process (e.g. resublimation)**



Fuel cell (schematic)

Ice crystal

1. Introduction

What is Photochemistry?

Definition

- **Photochemistry is concerned with changes in the chemical and physical behaviour of molecules following the absorption of one (or more) photons**

- **Photochemical reactions are primarily triggered by UV or visible radiation, although IR radiation can also influence chemical behavior**

- **Photochemical reactions are primarily triggered by electronic excitation, even if these are usually accompanied by excitation of vibrational states (as well as rotational states in the gas phase)**

Basic rules of photochemistry

1. **Only light that is absorbed causes photochemical processes (Grotthus, Draper)**
2. **A molecule that has absorbed a quantum of light enters an excited state (Stark, Einstein)**

1. Introduction

Photochemistry, among other Chemical Processes, i.e. Heterogeneous and Homogeneous Catalysis, Biocatalysis, Synthesis in Supercritical CO_2 or Ionic Liquids, etc., is the Basis of so-called Green Chemistry.

The terms green chemistry and photochemistry were coined around the same time, i.e. around 1900 (photochemical synthesis of vitamin D ~ 1927 by Adolf Windaus, Göttingen)

Green chemistry refers to synthesis techniques with the following characteristics:

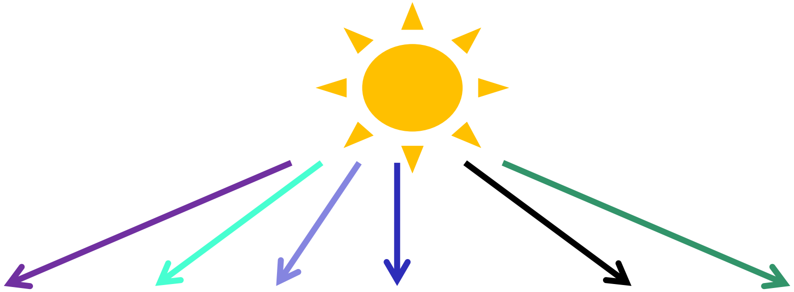
- **High energy efficiency**
- **Minimal or preferably no formation of waste**
- **Avoidance of toxic and/or hazardous solvents or reagents**
- **Use of renewable raw materials**

Photochemistry refers to synthesis techniques with the following characteristics

- **High energy efficiency**
- **High selectivity (if suitable radiation sources are used, e.g. monochromatic radiation ⇒ LED or laser diodes as disruptive radiation sources)**
- **Enables synthesis of complex products**
- **Avoidance of the use of hazardous oxidising agents, e.g., chromates**

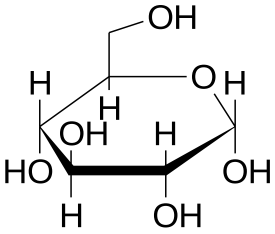
1. Introduction

Photochemistry in Nature



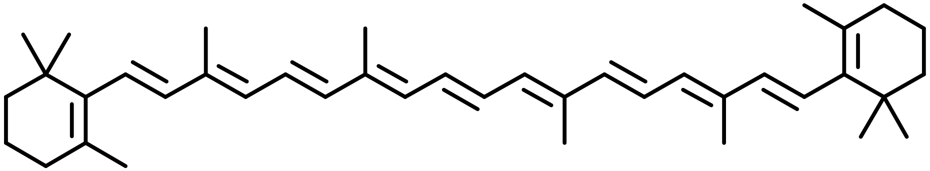
Photosynthesis

$6\,CO_2(g) + 6\,H_2O(g) \longrightarrow$

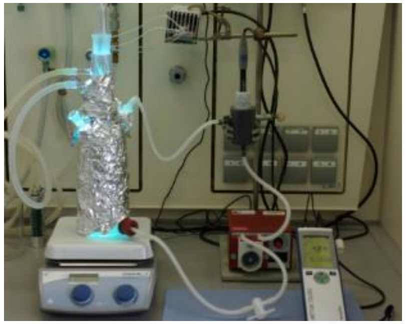


$+ 6\,O_2(g)$

Degradation of β-carotene & air pollutants



Technical

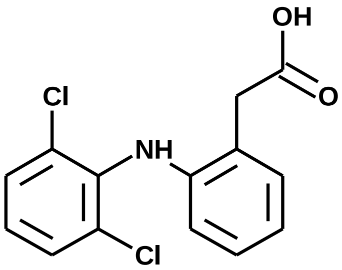


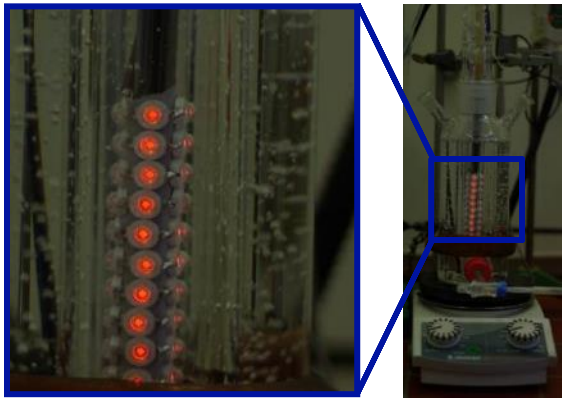
Surface coating with UV radiation

$2\,N_3^-(aq) + h\nu \rightarrow 3\,N_2(g) + 2\,e^-$

$2\,H_2O(l) + 2\,e^- \rightarrow 2\,H_2(g) + 2\,OH^-(aq)$

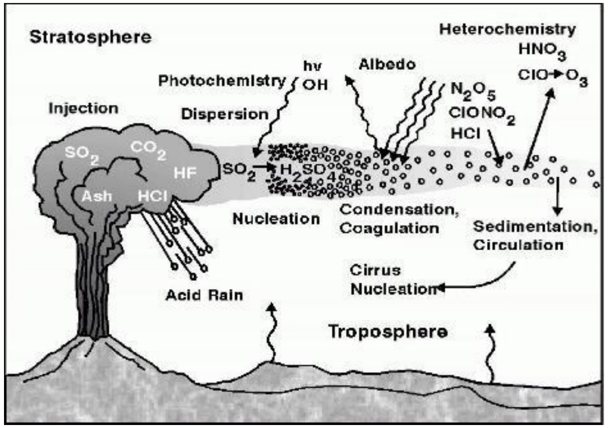
Degradation of diclofenac with NIR radiation





1. Introduction

Photochemistry - The Basis of Life



Atmosphere	**O_3-formation**
(Tropo- and stratosphere)	**Degradation of hydrocarbons**
	NO_x Forming (Fertiliser)
Hydrosphere	**H_2O_2 Splitting**
	Photocatalysis:
	$NO_2^- \rightarrow NO$
Biosphere	**Photosynthesis :**
	$6\ CO_2 + 12\ H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2 + 6\ H_2O$
	Photocatalysis :

Chemical industry	**Synthesis of speciality chemicals**
	Bleaching processes / cleaning
	Photopolymerization / polymer hardening
(Bio)medicine	**Therapy, e.g. PDT**
	NO (Pain therapy) and vitamin D formation
	Bilirubin breakdown
Semiconductor industry	**Photolithography**
	Ultra-pure water, ultra-pure surfaces
	Photochemical etching
Power generation	**Artificial photosynthesis : $2\ H_2O \rightarrow 2\ H_2 + O_2$**
	Solar cells (Graetzel cell): TiO_2 + Sensitiser + Redox mediator
Basic research	**Actinometry & dynamics of chemical processes**

1. Introduction

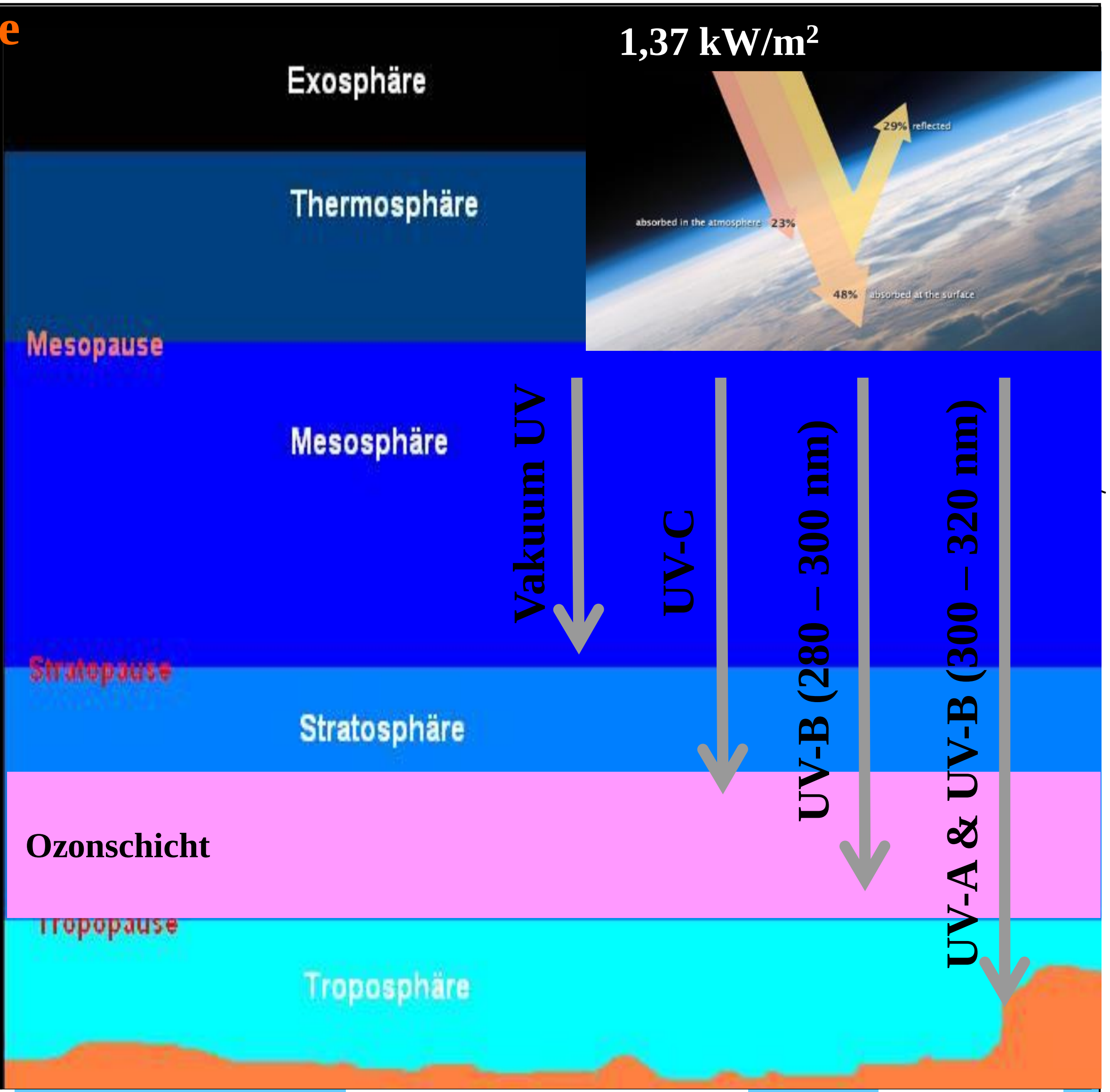
Photochemistry - The Basis of Life

Extreme UV (10 - 100 nm)
- Splitting of CH_4 and N_2
- Nitrile formation

Vacuum UV (100 - 200 nm)
- Photolysis of water, loss of H_2
- Splitting of N_2 and O_2
- Ozone formation

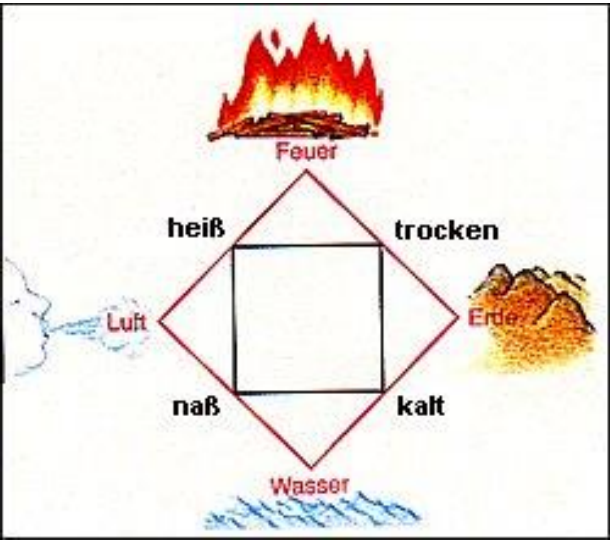
UV-C (200 - 280 nm) &
UV-B (280 - 300 nm)
- Ozone formation

UV-B (300 - 320 nm) &
UV-A (320 - 380 nm)
- Photochemical ageing
- Disinfection via photocatalysis



2. Historical Development

Water in Antiquity



Egypt

- Calendrical determination of the beginning of the Nile Flood
- Rise of the star Sirius (greek: Σωθις, Sothis,
  greek: Σείριος, Seirios)
- Introduction of water management ~ 3000 BC

Greece

- (Ἄριστον μὲν ὕδωρ: But the best thing is the water, Pindar, gr. Poet, 517-437 BC)
- Thales of Miletus : Water is a precondition for life
- Water as an element (associated with emotion and intuition, icosahedron)

Rome

- Fresh water supply via viaducts
- Rome, Segovia, Nimes, Cologne (Colonia) etc.
- Sewage disposal via cesspools (Mesopotamia, Indus Valley)

2. Historical Development

Water in the Modern Age

Henry Cavendish (1783)

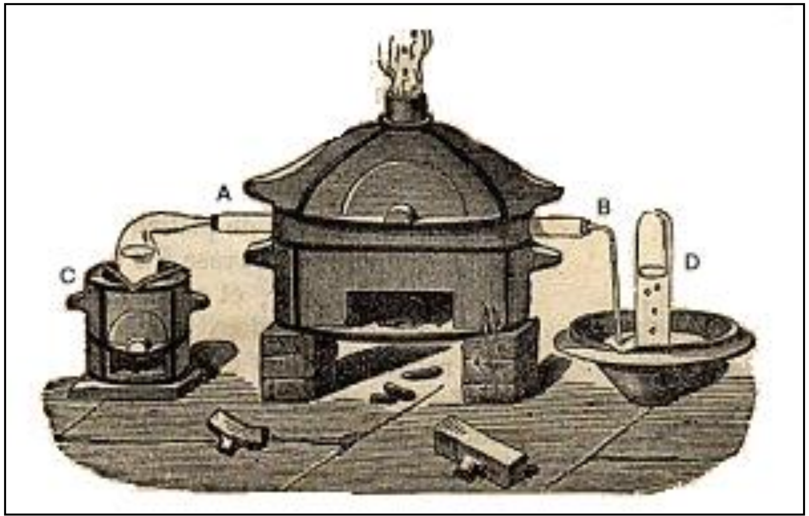
- Combustion of combustible air (H_2) produces water

Gaspard Monge, Antoine Laurent de Lavoisier und Pierre-Simon Laplace

- Water is a composite body (compound) of the "air inflammable" (H_2 gas) and the "air respirable" (O_2 gas)

Antoine Laurent de Lavoisier (1784)

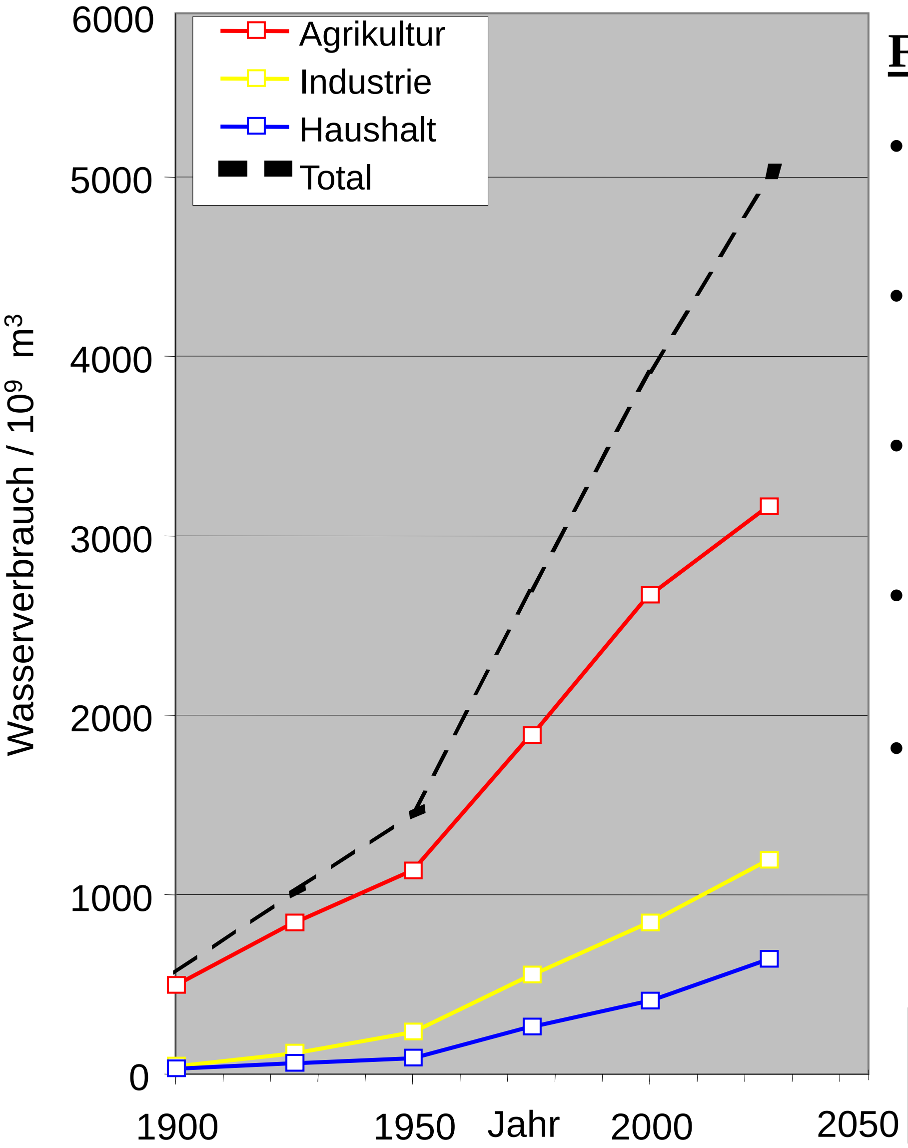
- Water is an oxide that can oxidize metals
- $3\ Fe(s) + 4\ H_2O(g) \rightarrow Fe_3O_4(s) + 4\ H_2(g)$



Jules Verne (1870)

- Water is the coal of the future → H_2

2. Historical Development



Facts and Figures

- In the last 100 years, global water consumption has grown twice as fast as the population
- 0.6% of globally available water reserves are suitable for drinking water
- 1.2 billion people have no access to safe drinking water
- 3 billion people suffer from diseases caused by contaminated drinking water
- Unclean water causes more than 2 million deaths a year, mostly among children

Growing demand for efficient and cost-effective water treatment technologies

2. Historical Development

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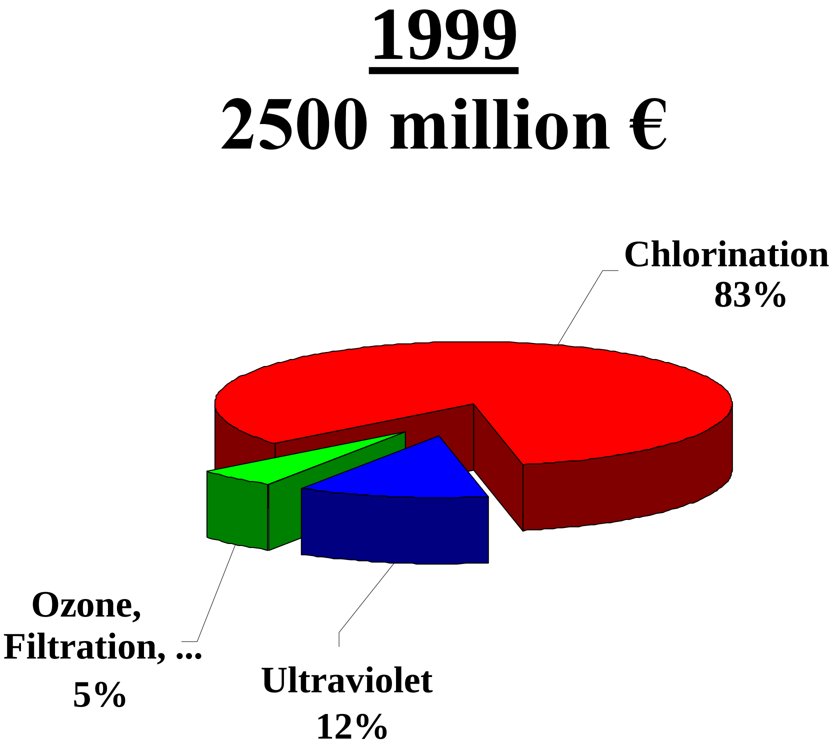
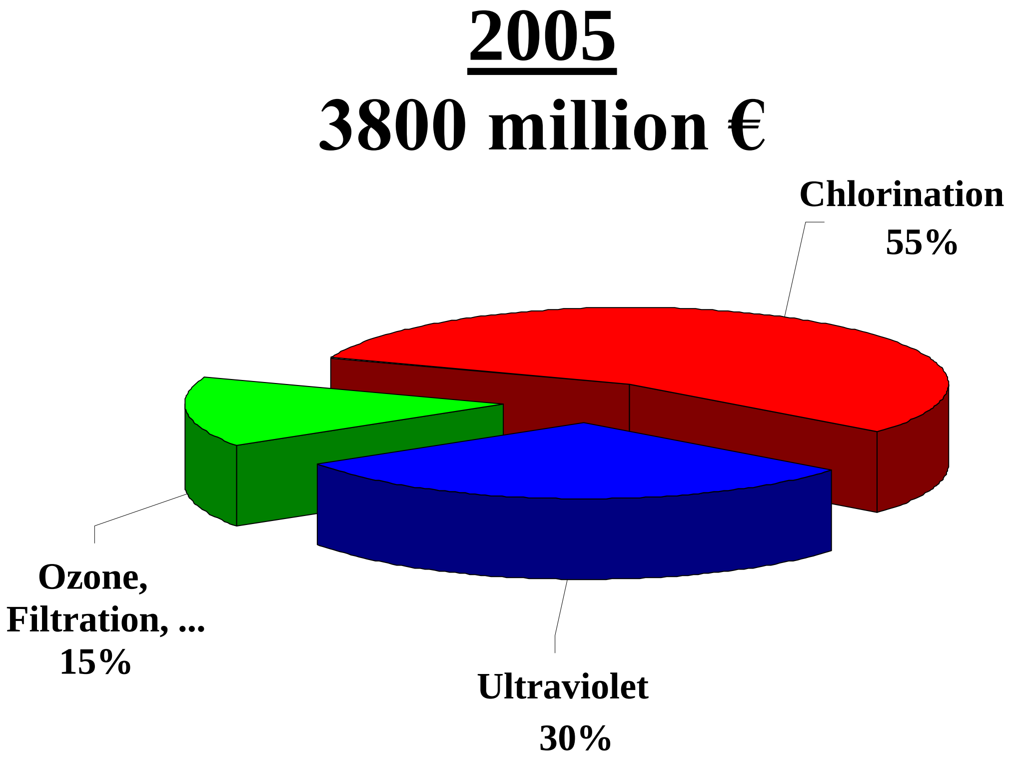




- Moderate growth of the overall market (7% p.a.)
- Strong tendency to replace chlorination with other processes
- The UV and ozone segment is growing at an above-average rate

3. Water Resources

Earth is a Water Planet

Surface area	$[10^6\ km^2]$	Share of land or sea [%]	Share of total Earth's surface [%]
Earth's surface	510	-	100
Seas	361	100	70.8
Arctic	12	3	2.4
Atlantic	94	26	18.4
Indian	74	21	14.5
Pacific	181	50	35.5
Continents	149	100	29.2
Africa	30	20	5.9
Antarctica	16	11	3.1
Asia	45	30	8.8
Australia/Oceania	8	5	1.5
Europe	10	7	2.0
North America	22	15	4.3
South America	18	12	3.5

Mass of the earth	$5.98 \cdot 10^{27}$ g
Mass of the hydrosphere	$1.66 \cdot 10^{24}$ g
Mass of the atmosphere	$5.14 \cdot 10^{21}$ g
Mass of the biosphere	$1.15 \cdot 10^{19}$ g

3. Water Resources

Water Occurs on Earth in all Aggregate States

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

Water supplies on earth ~ $1.38 \cdot 10^{18}$ m^3

Surface of the earth ~ $510 \cdot 10^{12}$ m^2

→ Average height of the water column ~ 2700 m

In addition, water occurs in bound form as water of crystallisation and as a solvent in all living organisms (plants, animals, microorganisms)

Lithosphere

Biosphere

(Water input from the cosmos ~ 2 million tons/year)

All life processes take place in an aqueous environment, i.e., biology can also be described as aquatic chemistry

Human body	65% H_2O
Some vegetables	90% H_2O

Drinking water $3.6 \cdot 10^{15}$ m^3 (0.27%)

3. Water Resources

Global Water Resources and Freshwater Availability

	Volume $[10^3\ km^3]$	Share of total volume [%]	Share of total Fresh water [%]	Renewal time [years]
Oceans	1370323	93.94	-	3000
Deep groundwater	60000	4.11	-	5000
Active groundwater	4000	0.27	14.09	330
Ice	24000	1.65	84.57	8000
Lakes	280	0.02	0.99	7
Soil moisture	85	0.01	0.30	1
Atmosphere	14	< 0.01	0.05	0.03
Rivers	1,2	< 0.01	< 0.01	0.03
Σ Fresh water	28380.2	1.95	100	-
Σ Water	1458703	100	-	-

	Africa	Asia	Australia/Oceania	Europe	North	South America
Share of available fresh water	11%	36%	5%	8%	15%	25%

4. Importance and Utilisation of Water

Water Plays a Central Role in Ecosystems of all kinds

- The presence of liquid water is a vital prerequisite for all life forms as we know them
- Water is an excellent solvent with high polarity
- Many other substances (nutrients, pollutants, gases, etc.) are transported with water
- Water vapor is a significant natural greenhouse gas
- The phase transitions of water convert large amounts of energy

Biology: Science of living systems

Medium: $H_2O(l)$ ⇒ Aquatic chemistry

⇒ Search for liquid H_2O (and its photolysis products O_2, O_3) on exoplanets

4. Importance and Utilisation of Water

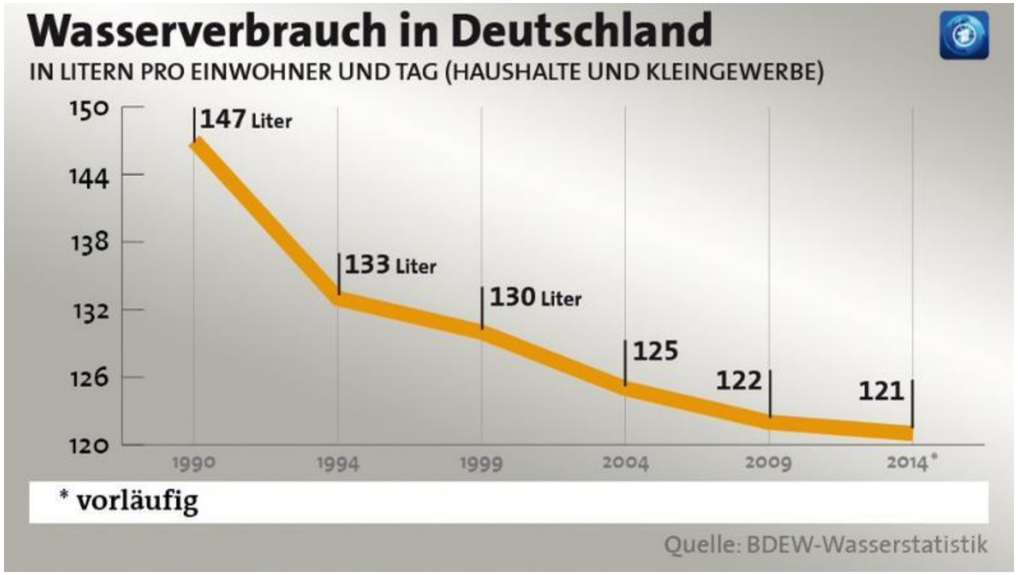
Daily Water Consumption

In Germany since 1990

- **Household consumption per person per day decreasing from 147 liters to 121 liters**
- **Including industrial consumption, around 220 liters per inhabitant per day**

Coverage

62%	Ground water
12%	Spring water
6%	Bank filtrate
20%	Surface water



* vorläufig

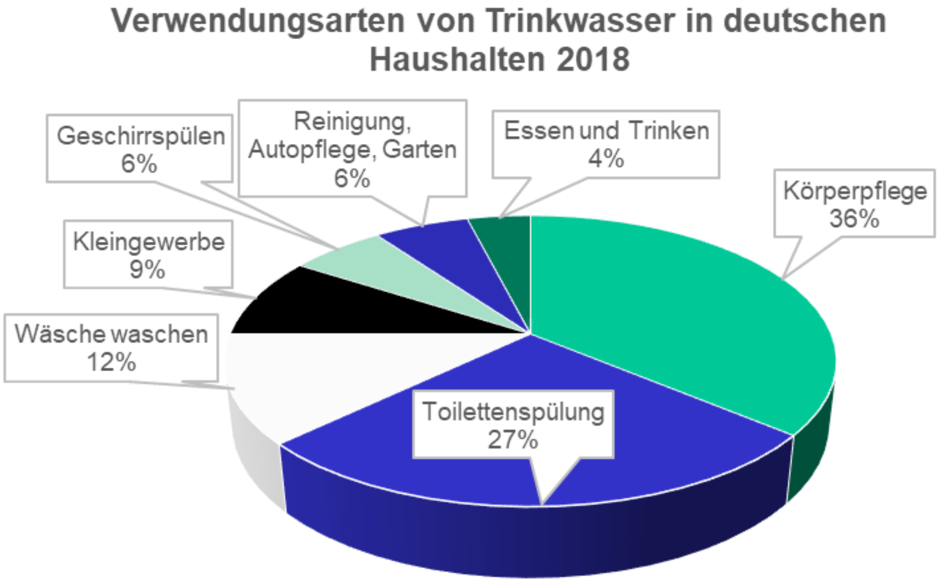
Quelle: BDEW-Wasserstatistik

4. Importance and Utilisation of Water

Daily Water Consumption

Breakdown of household consumption per person

• Toilet flush	46 l
• Bathing, showering	44 l
• Laundry	17 l
• Body care	9 l
• Dishwashing	9 l
• Watering the garden	6 l
• Car wash	3 l
• Cooking, drinking	3 l
• Other	8 l
Σ	145 l



4. Importance and Utilisation of Water

Water is the Ultimate Solvent for Biology, Chemistry & Industry

Elutrope Series

n-Hexane	$\varepsilon_r = 1.89$	Pyridin	$\varepsilon_r = 13.2$
n-Heptane	$\varepsilon_r = 1.94$	1-Butanol	$\varepsilon_r = 17.5$
n-Octane	$\varepsilon_r = 1.96$	2-Propanol	$\varepsilon_r = 20.2$
Cyclopentane	$\varepsilon_r = 1.97$	Acetone	$\varepsilon_r = 21.5$
Cyclohexane	$\varepsilon_r = 2.02$	Ethanol bei 20 °C	$\varepsilon_r = 25.8$
1,4-Dioxane	$\varepsilon_r = 2.24$	Methanol bei 25 °C	$\varepsilon_r = 33.8$
Tetrachlormethane	$\varepsilon_r = 2.24$	Nitrobenzol	$\varepsilon_r = 34.8$
Benzol	$\varepsilon_r = 2.28$	Acetonitrile	$\varepsilon_r = 37.5$
Toluene	$\varepsilon_r = 2.39$	Dimethylformamide	$\varepsilon_r = 37.7$
Chlorobenzene	$\varepsilon_r = 5.64$	Nitromethane	$\varepsilon_r = 38.6$
Diethylether	$\varepsilon_r = 4.34$	Dimethylsulfoxide	$\varepsilon_r = 40.7$
Chloroform	$\varepsilon_r = 4.81$	Water at 40 °C	$\varepsilon_r = 73.8$
Tetrahydrofuran	$\varepsilon_r = 7.52$	Water at 18 °C	$\varepsilon_r = 81.1$
Chinolin	$\varepsilon_r = 9.0$	Water at 0 °C	$\varepsilon_r = 88.0$
Dichlormethane	$\varepsilon_r = 9.08$	Aqueous buffer solutions	$\varepsilon_r > 81$

5. Physical Properties

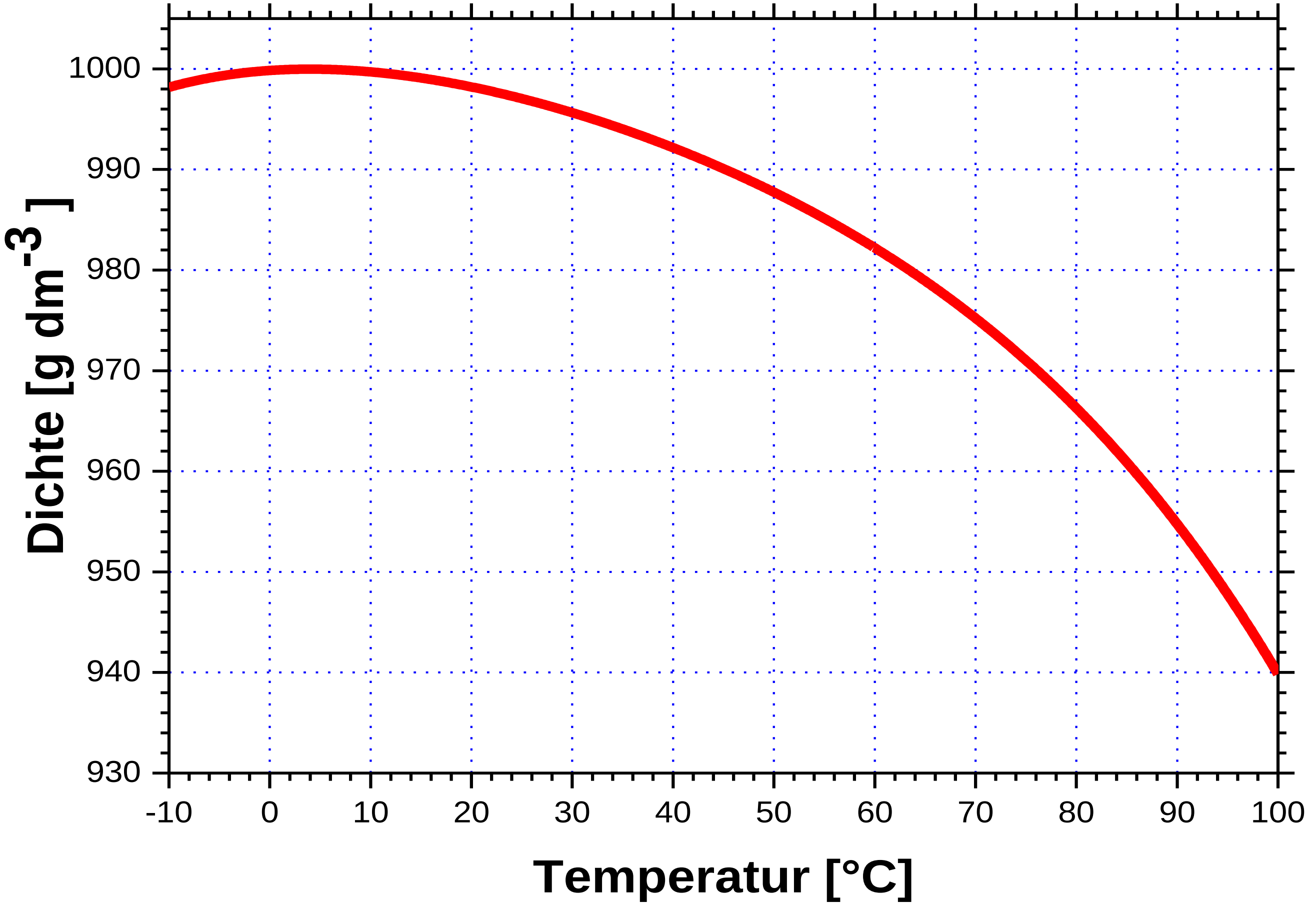
Overview

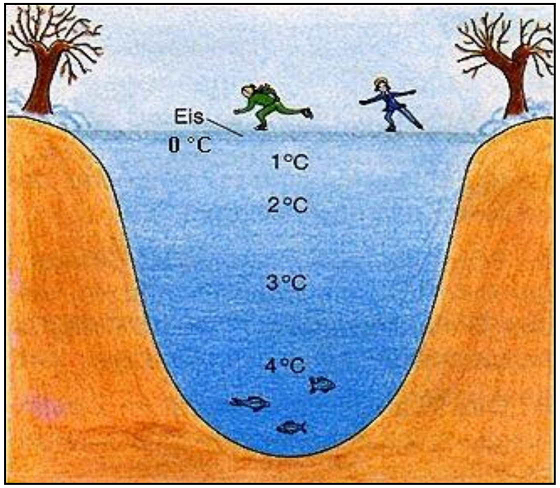
Size	Formula symbol	Value	Unit	Remark
Density	ρ	≤ 1	$g\ cm^{-3}$	Density anomaly !
Specific heat capacity	c_p	4216	$J\ kg^{-1}\ K^{-1}$	Very high!
Heat of vaporisation with RT	$\Delta^g{}_l H_m$	$2.495 \cdot 10^6$	$J\ kg^{-1}$	$2.5001 \cdot 10^6$ at 0 °C $2.26 \cdot 10^6$ at 100 °C
Melting heat	$\Delta^s{}_l H_m$	$3.3 \cdot 10^5$	$J\ kg^{-1}$	
Surface tension	σ	0.076	$N\ m^{-1} = J\ m^{-2}$	at 0 °C

5. Physical Properties

Density of Liquid Water

The density of water at 0 °C is almost 1 kg dm^{-3}





Calculation according to Paul 1985:
http://www.tu-dresden.de/fghhihb/petzoldt/dichte_de.html

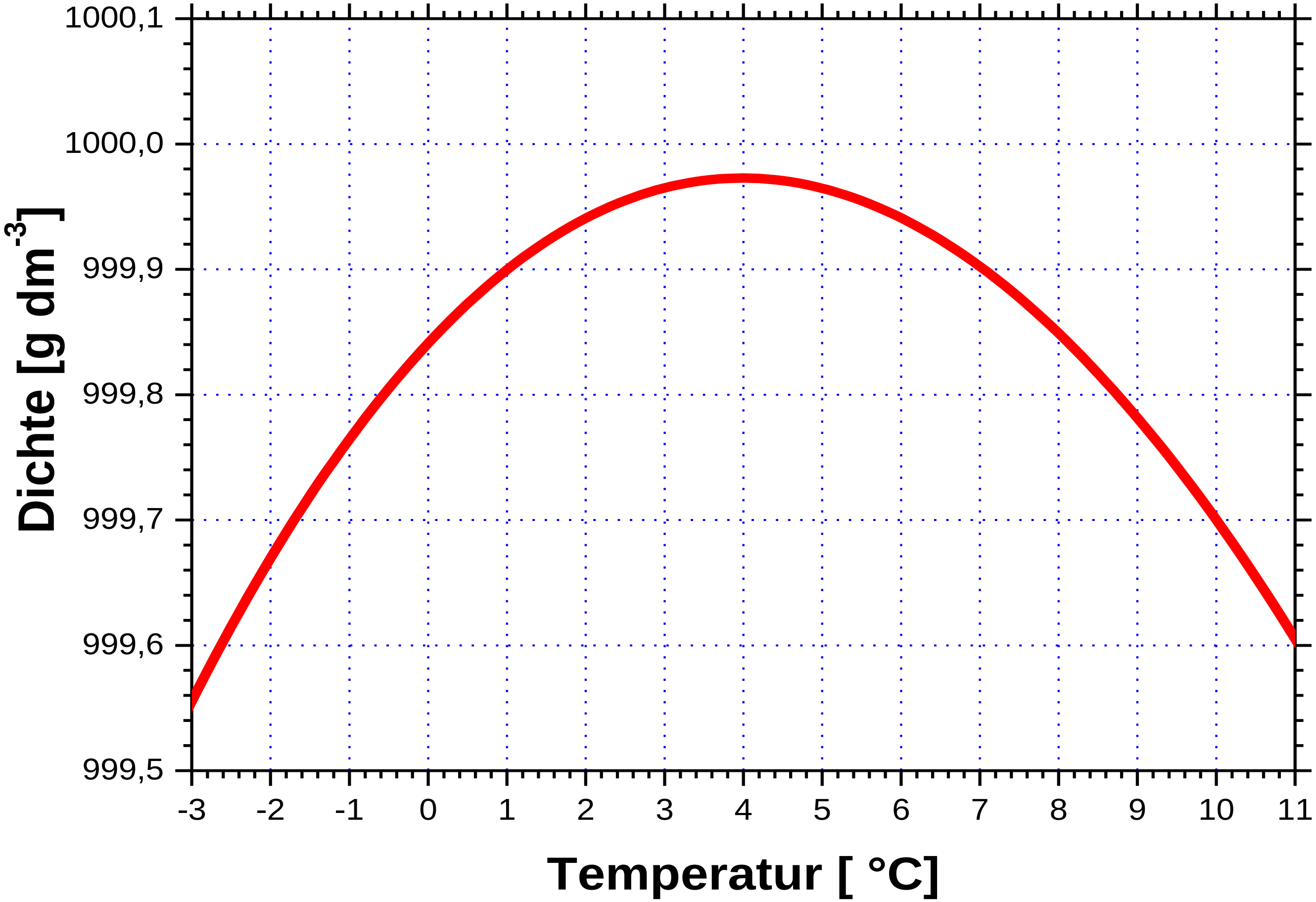
5. Physical Properties

Density of Liquid Water

Due to the density anomaly of water, the density is greatest at 4 °C Ice (without air inclusion) has a density at 0 °C of 916.8 g dm^{-3}

Consequences

- Ice floats on water
- Waters do not freeze to the bottom
- Ice formation cracks rocks



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http://www.tu-dresden.de/fghhihb/petzoldt/dichte_de.html

5. Physical Properties

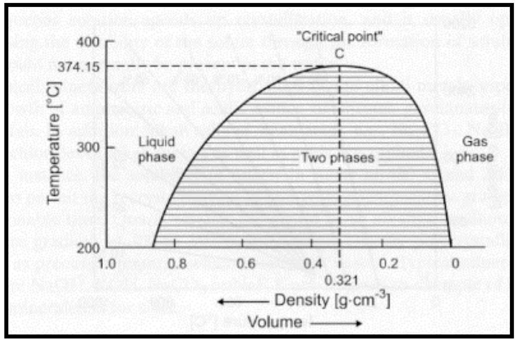
State Diagram of the Water

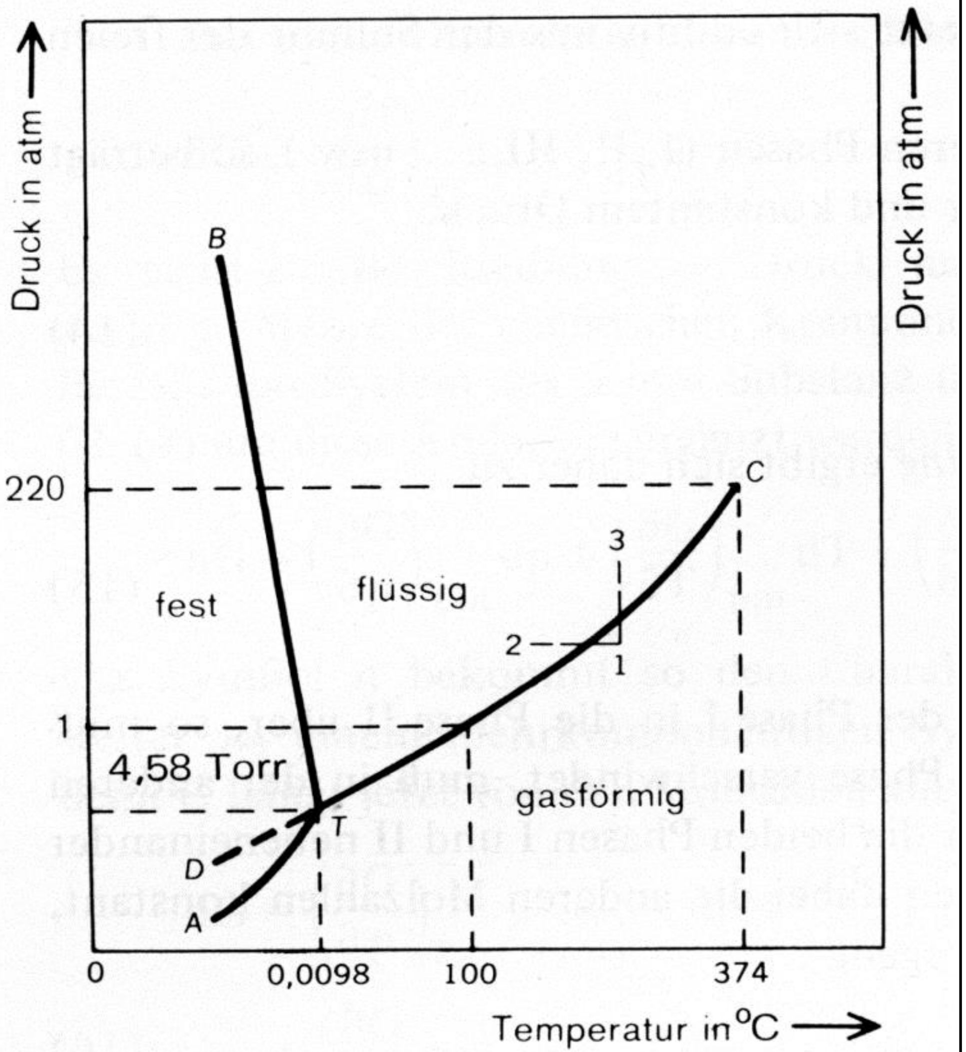
Triple point T at

- T_T = 0.01 °C
- P_T = 611.66 Pa (4.58 Torr ~ 6 mbar)

Critical point C

- T_C = 374.15 °C
- P_C = 220 bar
- Critical density = 0.321 gcm^{-3}

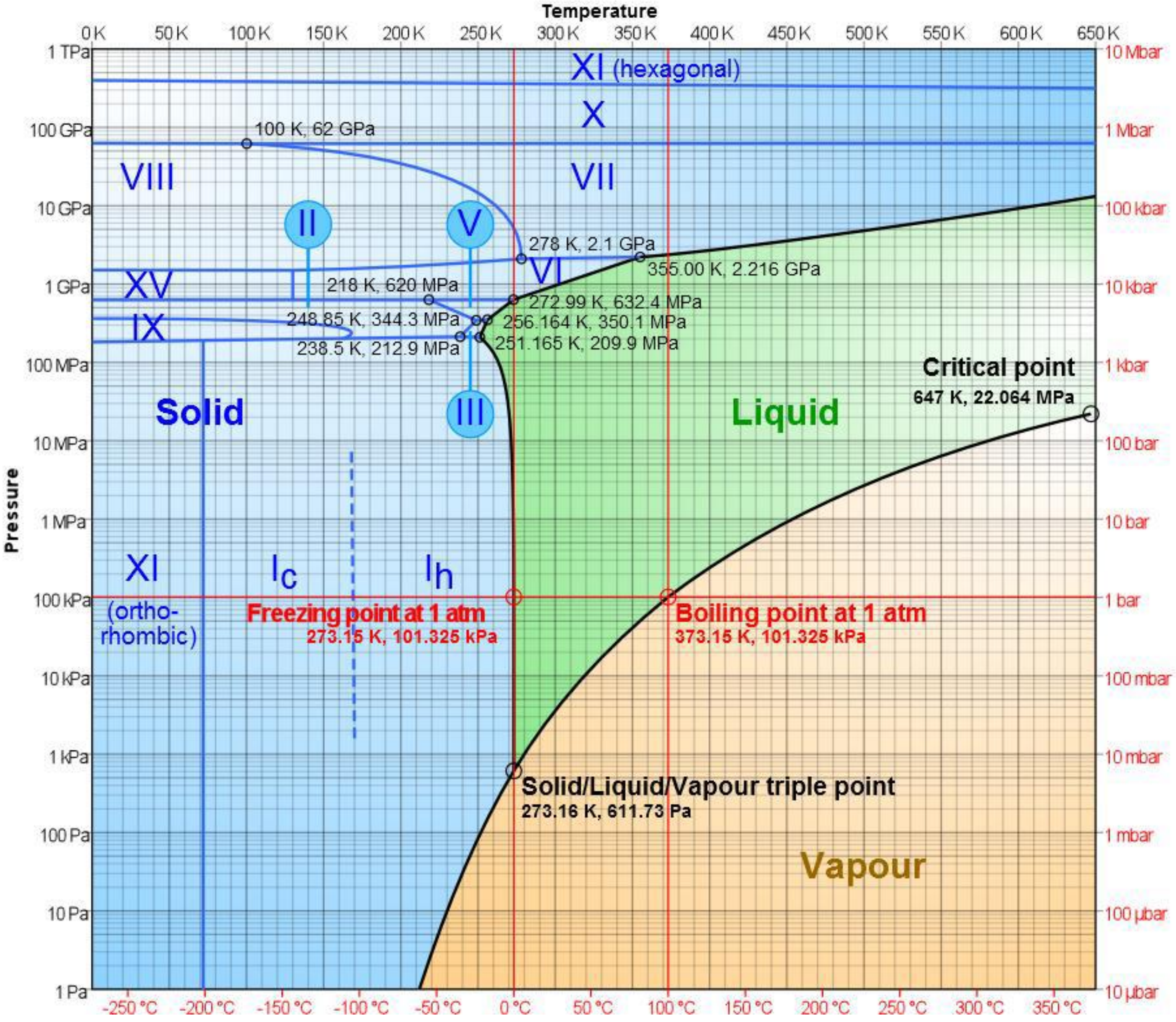




Source: Barrow, Physikalische Chemie, 1984

5. Physical Properties

State Diagram of the Water



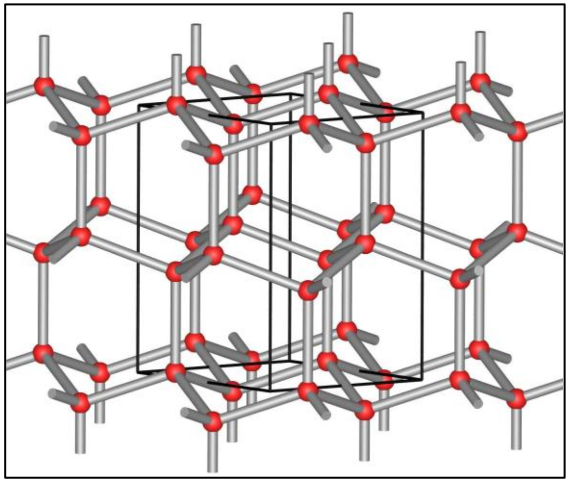
<u>**15 known ice phases to date**</u>

- **Amorphous**
- **I_h: hexagonal structure, practically all the ice in the Earth's biosphere**
- **I_c: cubic structure, oxygen atoms in diamond structure, possibly in the Earth's upper atmosphere**
- **II: rhombohedral, very ordered, probably present in icy moons**
- **III: tetragonal, lowest density of high-pressure ice**
- **IV: rhombohedral, important nucleation nuclei**

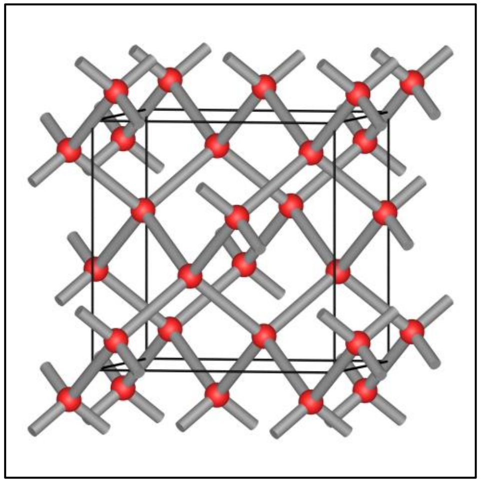
5. Physical Properties

Structure of the Ice Phases of Water

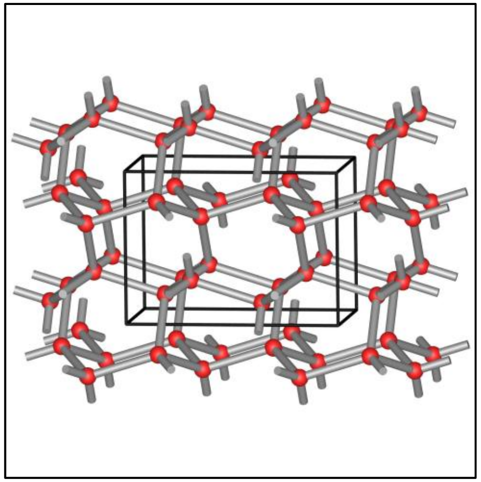
I_h: hexagonal (Tridymit)
$\rho = 0.92\ g/cm^3$



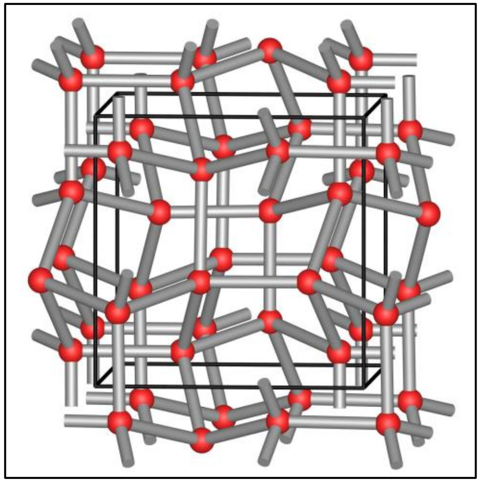
I_c: cubic (Cristobalit)
$\rho = 0.92\ g/cm^3$



II: rhombohedral (distorted Tridymit)
$\rho = 1.16\ g/cm^3$



III: tetragonal (Keatit)
$\rho = 1.17\ g/cm^3$

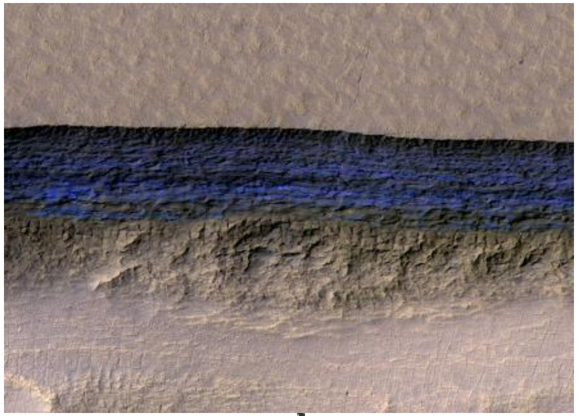


5. Physical Properties

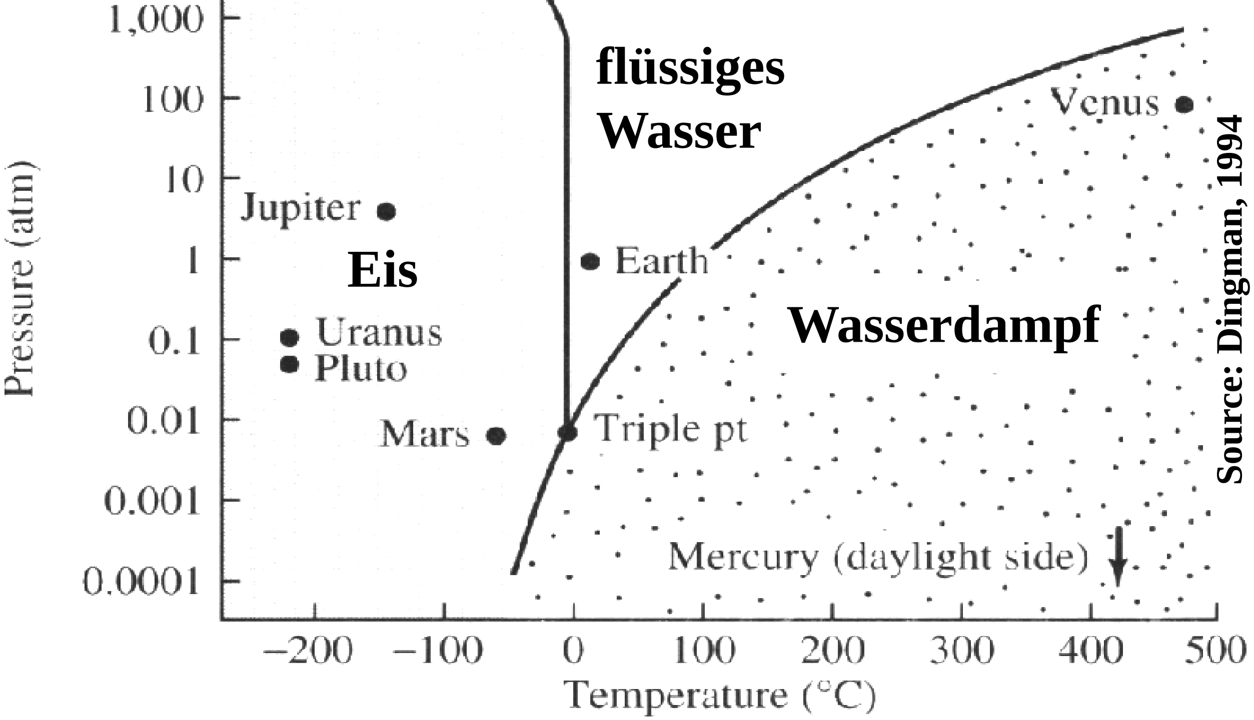
State Diagram of the Water

Phase state of water on solar planets and moons

Mercury	**g**
Venus	**g**
Earth	**s, l , g**
Mars	**s, g**
Ganymed	**s**
Europe	**s, l**
Titanium	**s**
Enceladus	**s, l**



Cross section through the surface of Mars (NASA)

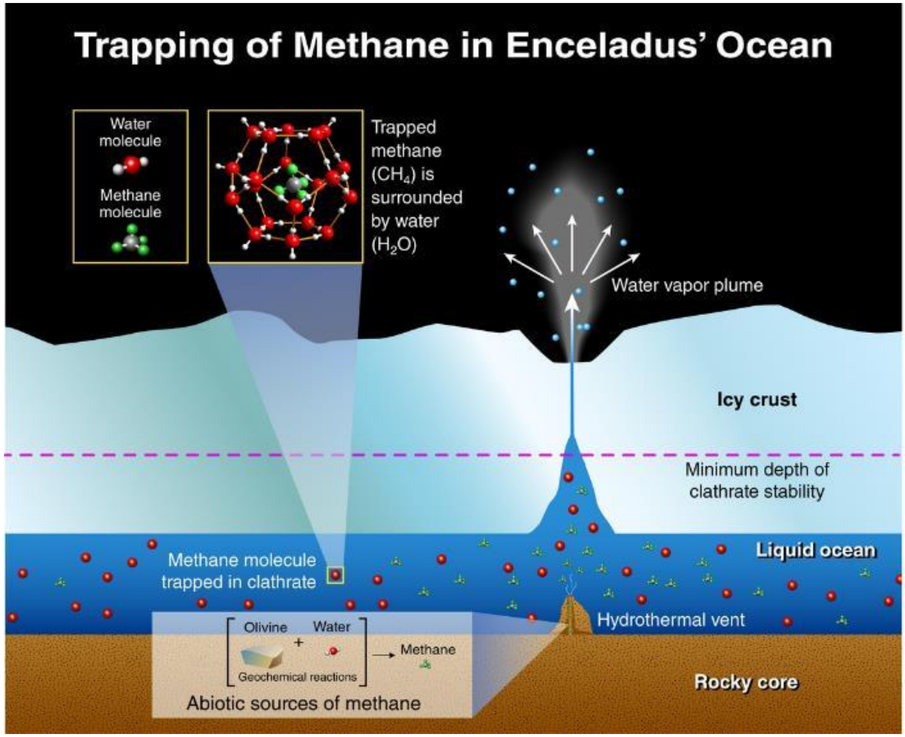


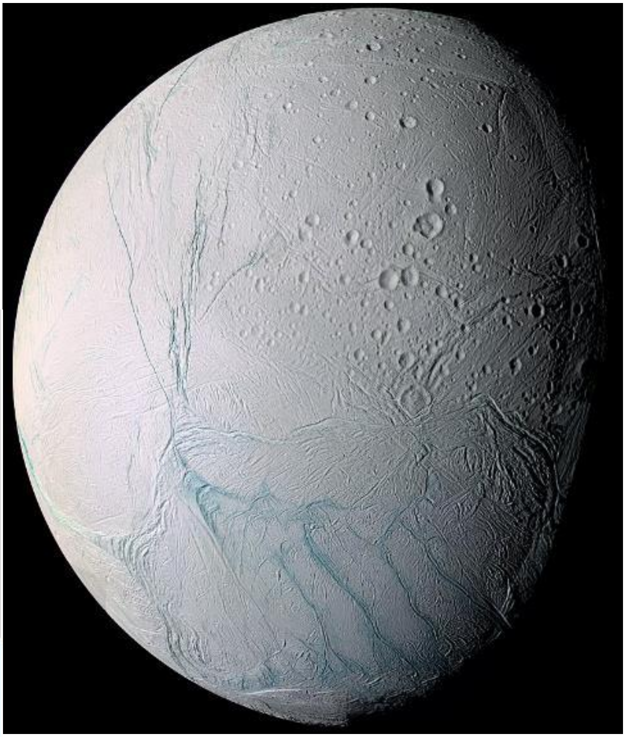
Source: Dingman, 1994

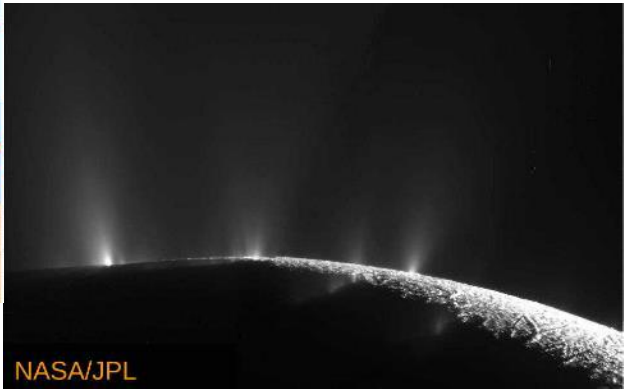
5. Physical Properties

Cryovolcanism on Enceladus (Saturn‘s Moon)

- T ~ 33 - 145 K (-240 bis -128 °C)
- Atmosphere (in Vol-%):
  91% H_2O
  4% N_2
  3.2% CO_2
  1.7% CH_4
- Formation of methane hydrate under the ice crust?
- Tidal friction as an internal energy source = f (distance to Saturn)



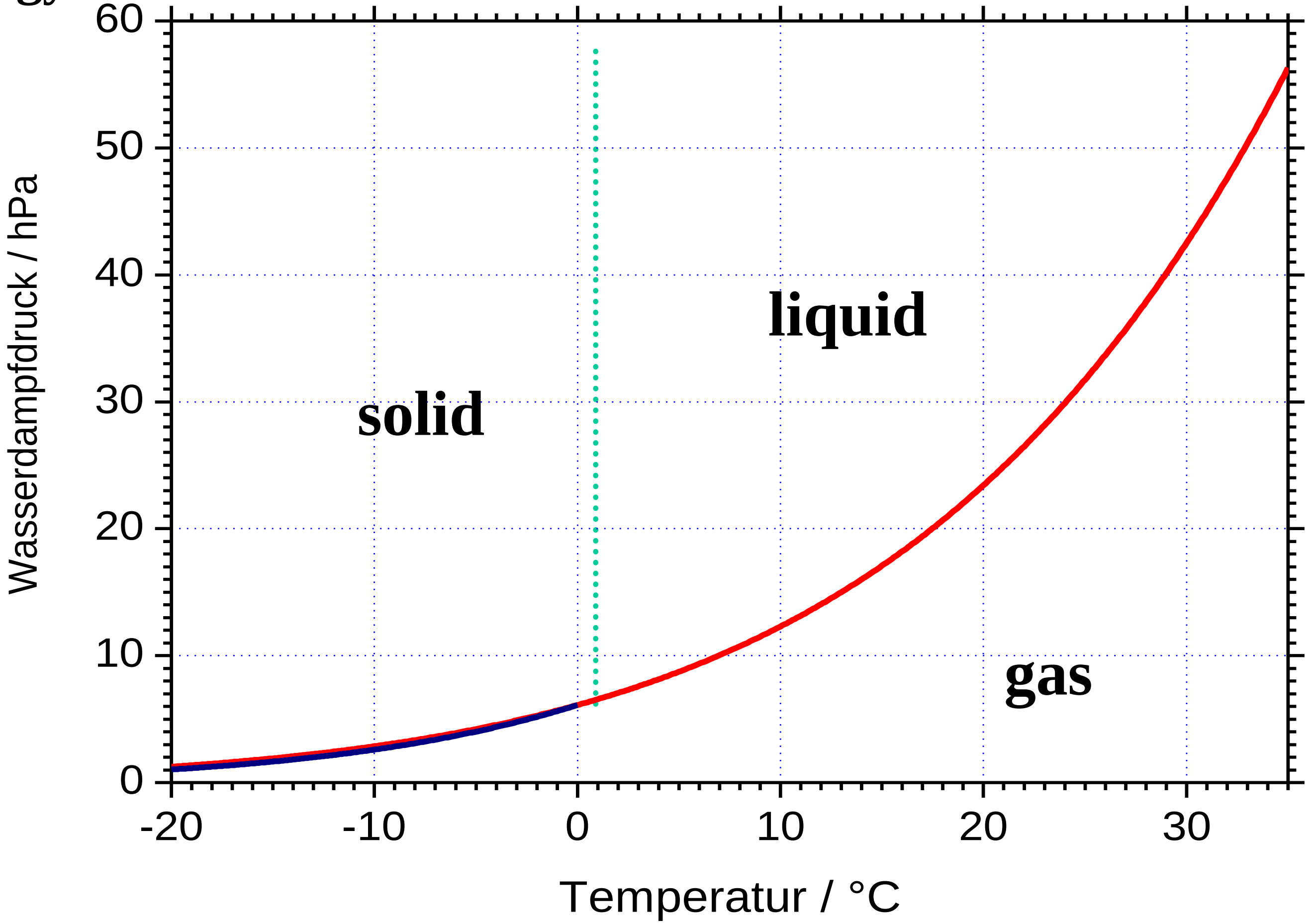




5. Physical Properties

State Diagram of the Water

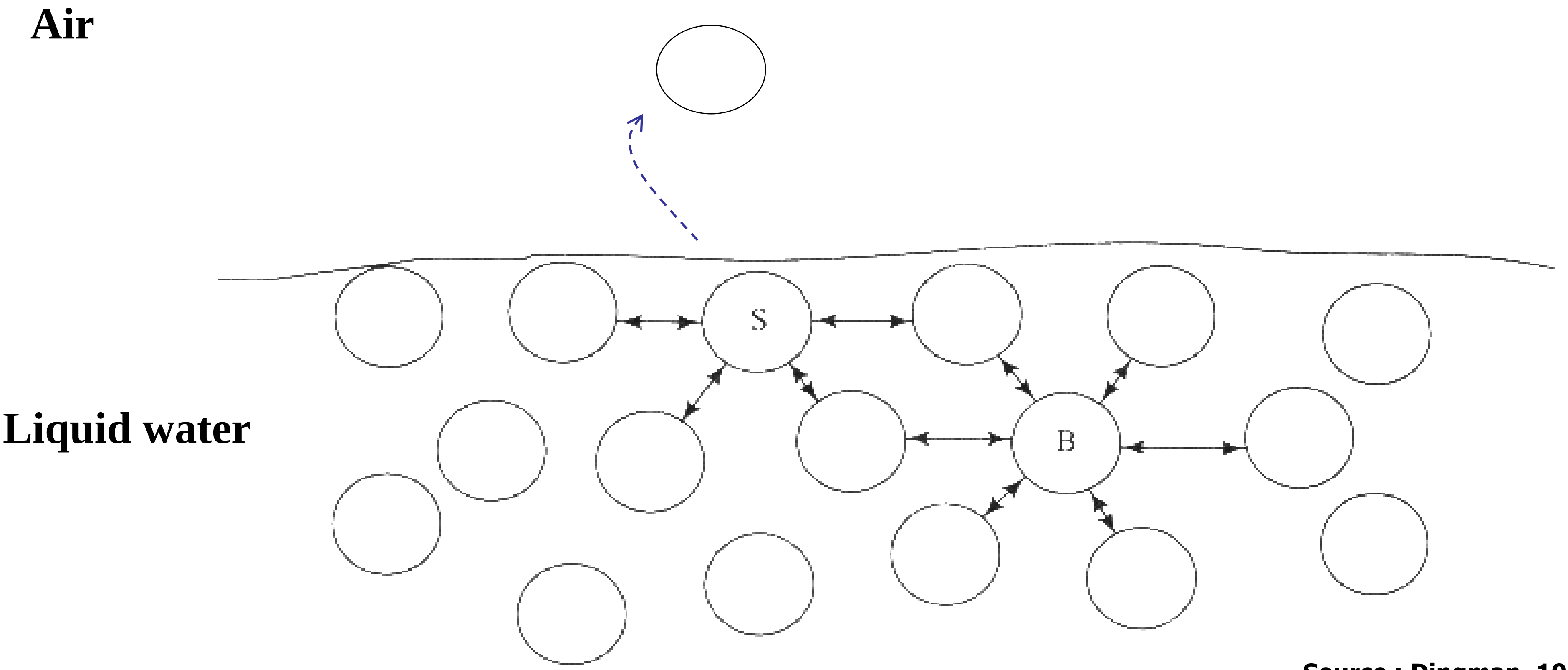
In the field of meteorology particularly interesting range, i.e. -20 to +35 °C



5. Physical Properties

State Diagram of the Water

Water molecules in the gas phase are in equilibrium with the liquid water
→ (equilibrium) water vapor pressure above the water surface

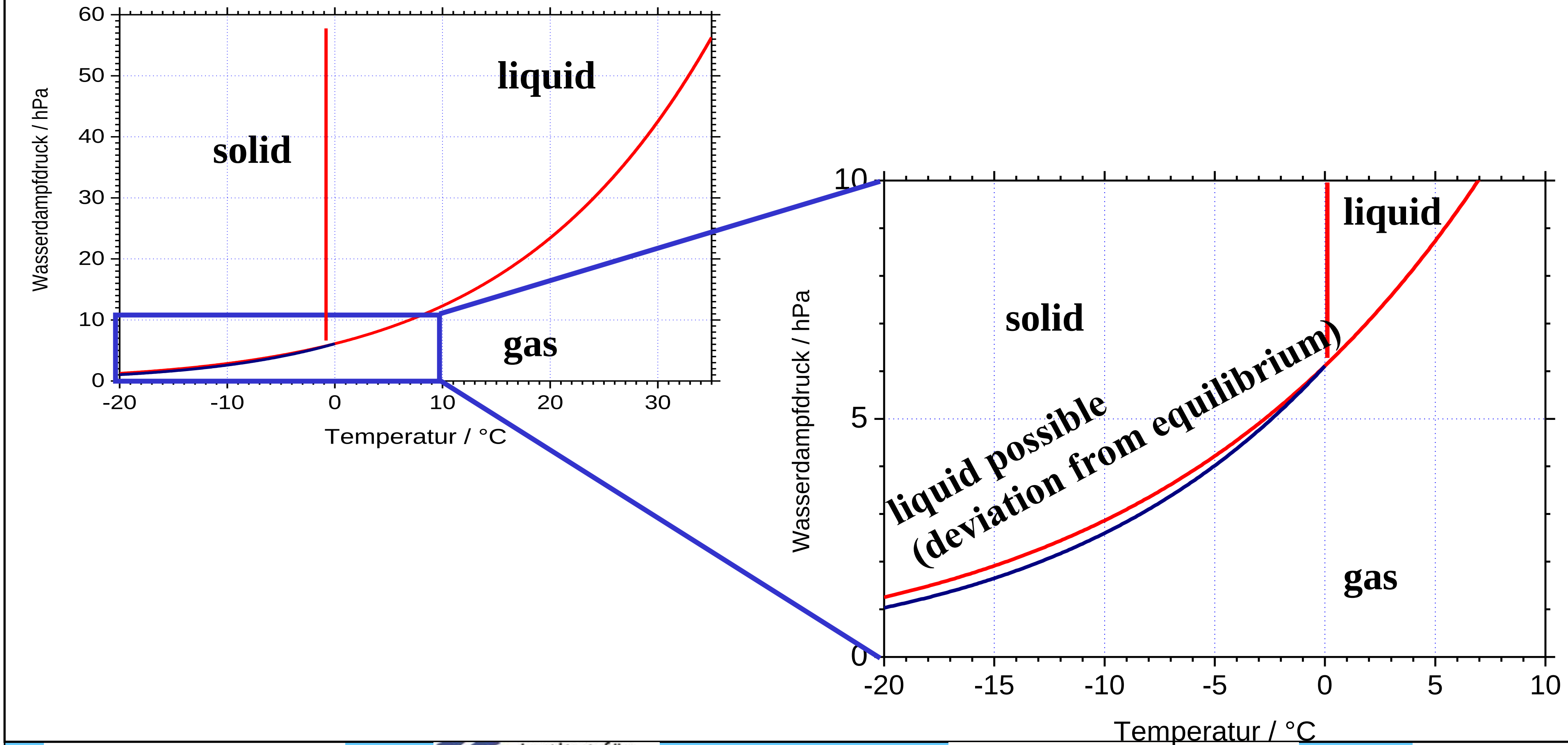


Source : Dingman, 1994

5. Physical Properties

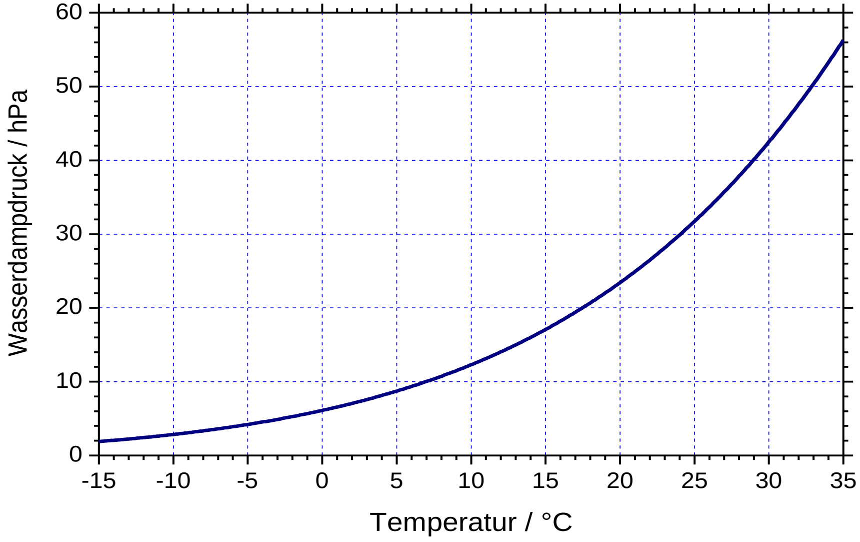
State Diagram of Water - deviation from Equilibrium

Supercooled liquid water: inhibition of crystallization due to more difficult nucleat.



5. Physical Properties

The Vapour Pressure Curve is described by the Clausius-Clapeyron Equation



Derivation of the Clausius-Clapeyron equation : (Cl.-Cl.-Gl.)

$$dG_m^{\,l} = dG_m^{\,g}$$

$$\Rightarrow -S_m^{\,l}\,dT + V_m^{\,l}\,dp = -S_m^{\,g}\,dT + V_m^{\,g}\,dp$$

$$\Rightarrow dp/dt = (S_m^{\,g}-S_m^{\,l})/(V_m^{\,g}-V_m^{\,l}) = \Delta^g{}_l S_m/(V_m^{\,g}-V_m^{\,l})$$

$$\Rightarrow \frac{dp}{dT} = \frac{\Delta_l^g H_m}{(V_m^g - V_m^l)T}$$

General Cl.-Cl.-Eq. nach $\Delta^g{}_l S_m = \Delta^g{}_l H_m / T$

$$\Rightarrow \frac{dp}{p} = \frac{\Delta_l^g H_m}{R}\,\frac{dT}{T^2}$$

Special Cl.-Cl.-Eq. (Approach: $V_m^{\,g} >> V_m^{\,l}$ und $V_m^{\,g} = RT/p$)

Phase	t (°C)	C_1 / hPa	C_2	C_3 / °C
Ice	< 0	6.11	22.44	272.44
Water	< 0	6.11	17.84	245.43
Water	> 0	6.11	17.08	234.18

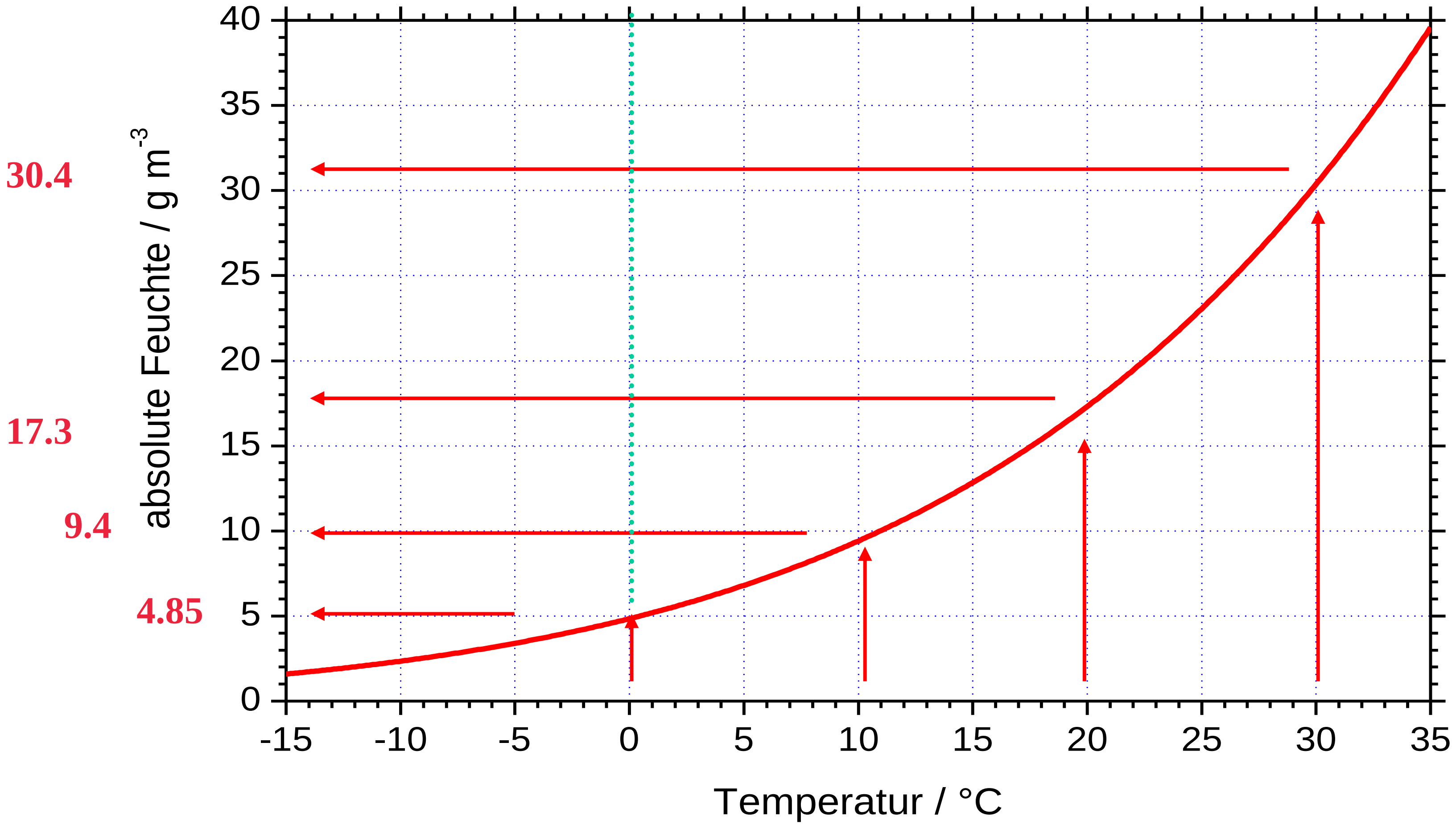
Approximation using the Magnus formula:

$$\boxed{p^*(t) = C_1 \cdot \exp\left(\frac{C_2 \cdot t}{C_3 + t}\right)}$$

p*: Saturation water vapor pressure; $\Delta^g{}_l H_m$: Heat of vaporisation
T: Temperature in K; t: Temperature in °C

5. Physical Properties

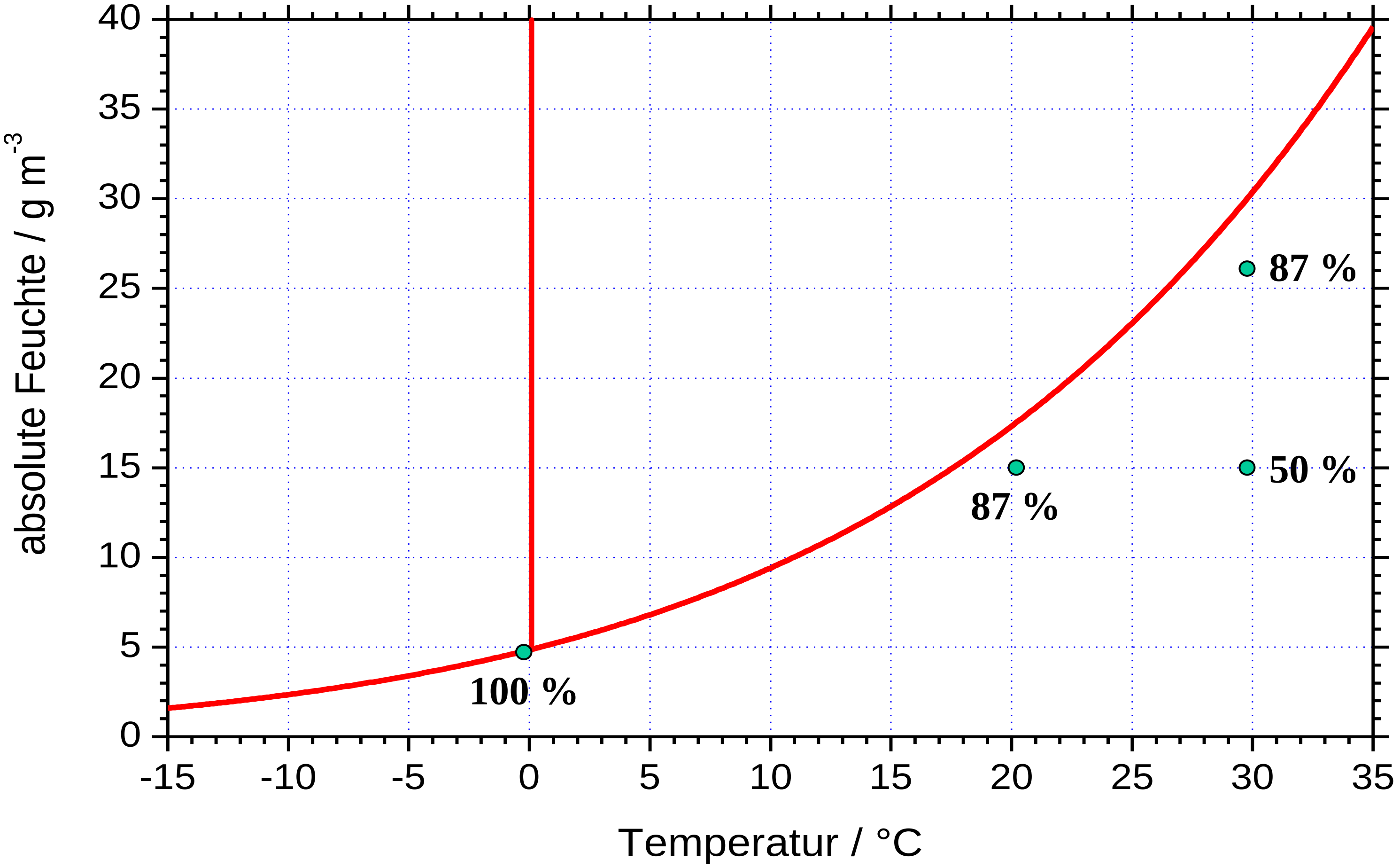
Water Vapour in the Air



Saturation curve for the water vapor content in air above liquid water (equilibrium curve). The curve corresponds to a relative humidity of 100 %.

5. Physical Properties

Water Vapour in the Air



The relative humidity rH is the ratio of the current moisture content / maximum possible moisture content or the water vapor pressure p / saturation vapor pressure p*

5. Physical Properties

Gases (CO_2, O_2, N_2, ...) Physically dissolve in Water

The gas solubility is described by the Henry constant K_H

$$\boxed{K_H = \frac{[X]}{p}}$$

K_H^X is the Henry constant for the gas X — Unit typically: mol l^{-1} hPa^{-1}

p is the partial pressure of the gas in the air — Unit: hPa

Henry constants for oxygen and for carbon dioxide in water at 25 °C:

$$K_H^{O_2} = 1.26 \cdot 10^{-6} \text{ mol l}^{-1} \text{ hPa}^{-1} \qquad K_H^{CO_2} = \frac{H_2CO_3^*}{p_{CO_2}} = 34 \cdot 10^{-6} \text{ mol l}^{-1} \text{ hPa}^{-1}$$

CO_2 dissolves about 25 times better in water than oxygen!

Note: The solubility of a gas in water increases with decreasing temperature!

5. Physical Properties

Gases - Rules for Physical Solubility in Water

- High pressure and low temperatures favor the process of absorption into the liquid phase (e.g. O_2 entry)
- Low pressure and high temperatures are favorable for gas discharge from the liquid phase

Gas	Partial pressure p_i [bar]	Temperature T [°C]	Saturation concentration [mol/m³]	[mg/l]
N_2	0.781	10	0.647	18.11
		25	0.505	14.13
O_2	0.209	10	0.35	11.2
		25	0.261	8.35
CO_2	0.0004 (rising)	10	0.0184	0.808
		25	0.0117	0.515

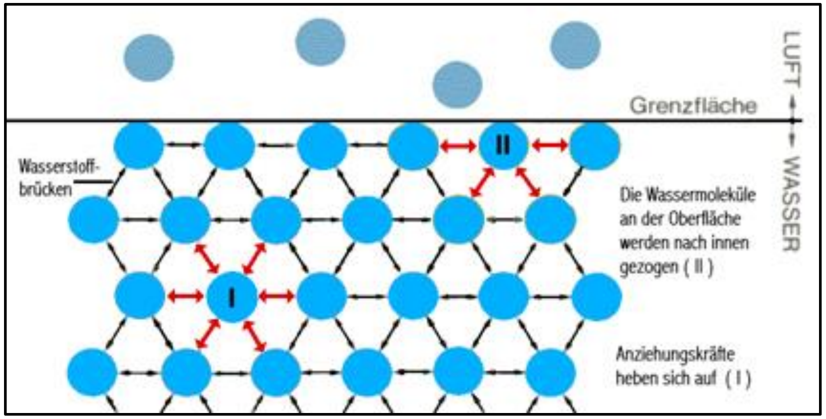
5. Physical Properties

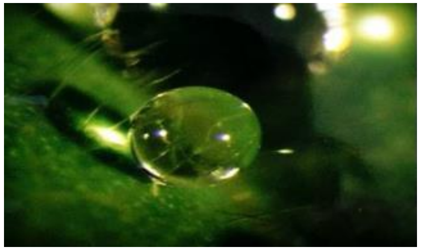
Surface Tension

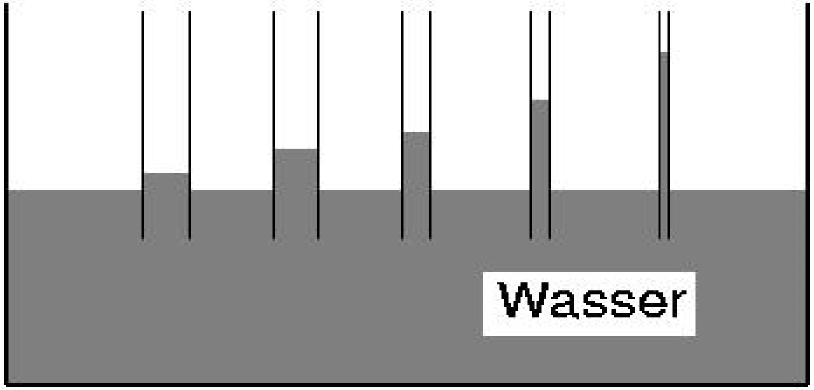
Cause: Strong intermolecular forces
1. In water, the forces act equally from all sides
2. At the surface, the molecules are only drawn into the liquid on one side

The greater the surface tension, the more the liquid endeavors to take on a spherical shape

<u>Effects</u>
- Small animals, such as water striders, can move on the water surface
- Rise of water in narrow tubes (capillaries): Supply of plants with water from the roots
- Limited wetting of surfaces: Detergents reduce surface tension





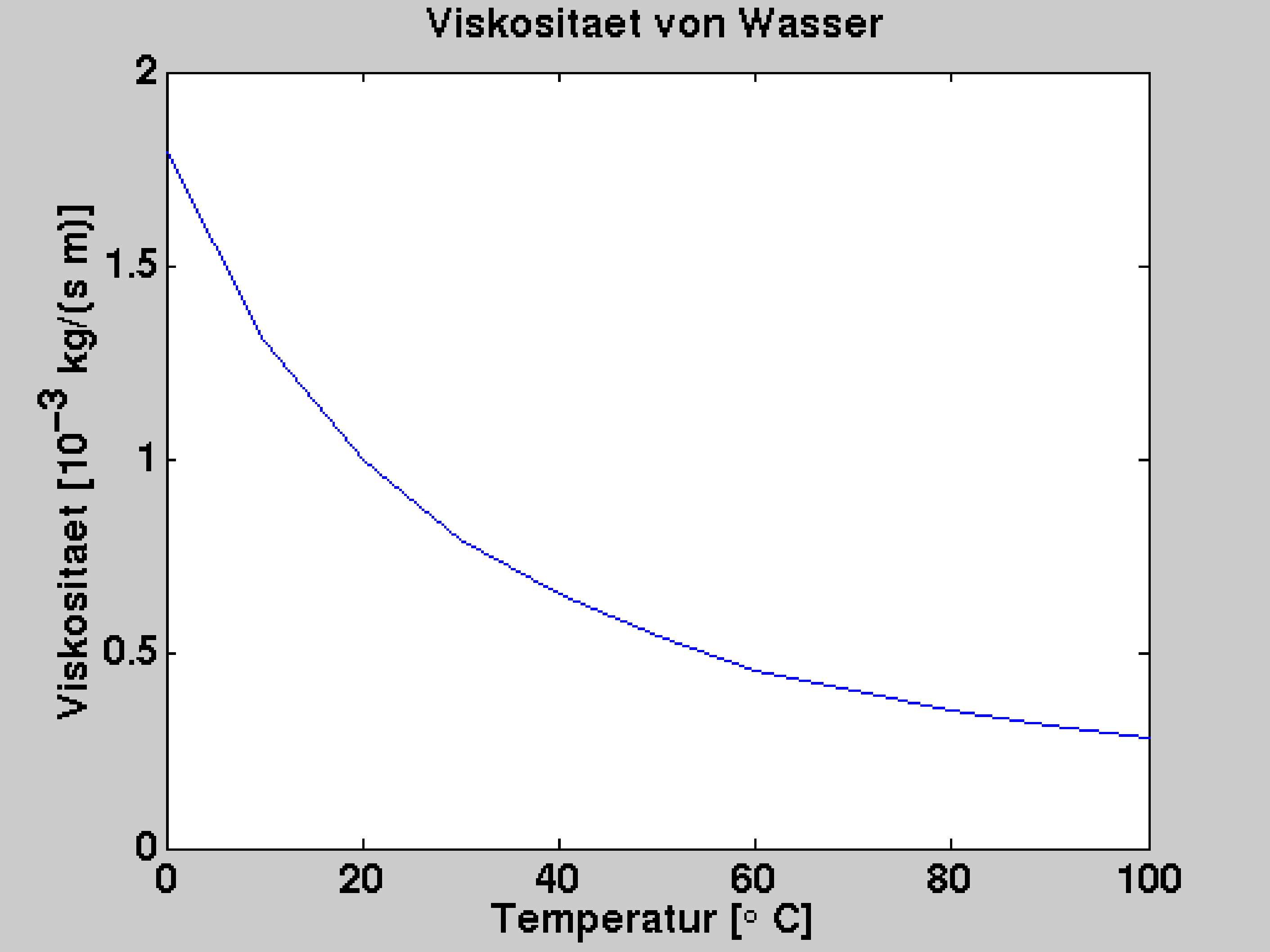


5. Physical Properties

Viscosity

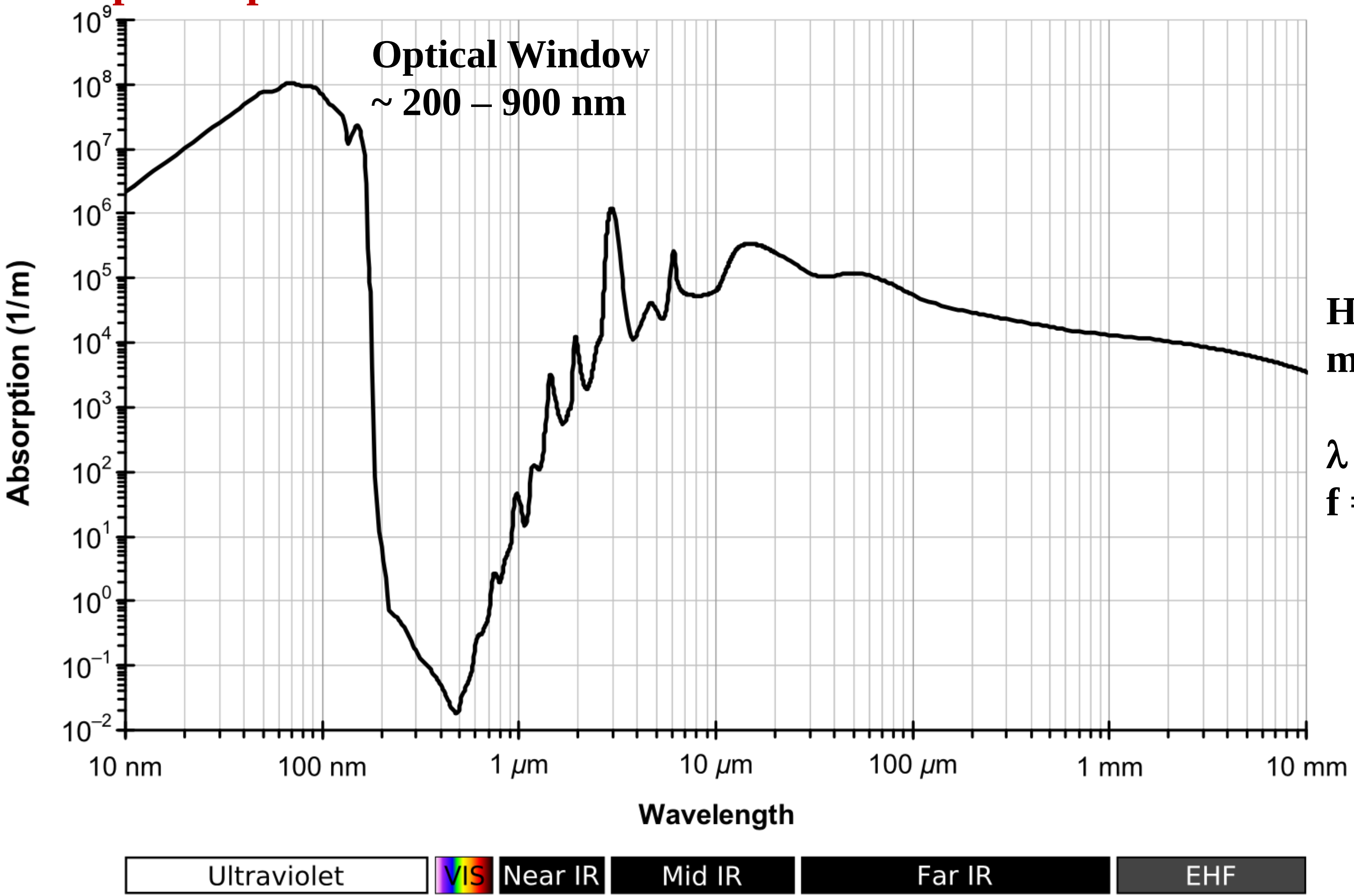
At room temperature

$0.8903 \cdot 10^{-3}$ $kgm^{-1}s^{-2}$



5. Physical Properties

Absorption Spectrum



Optical Window
~ 200 – 900 nm

Household microwave:

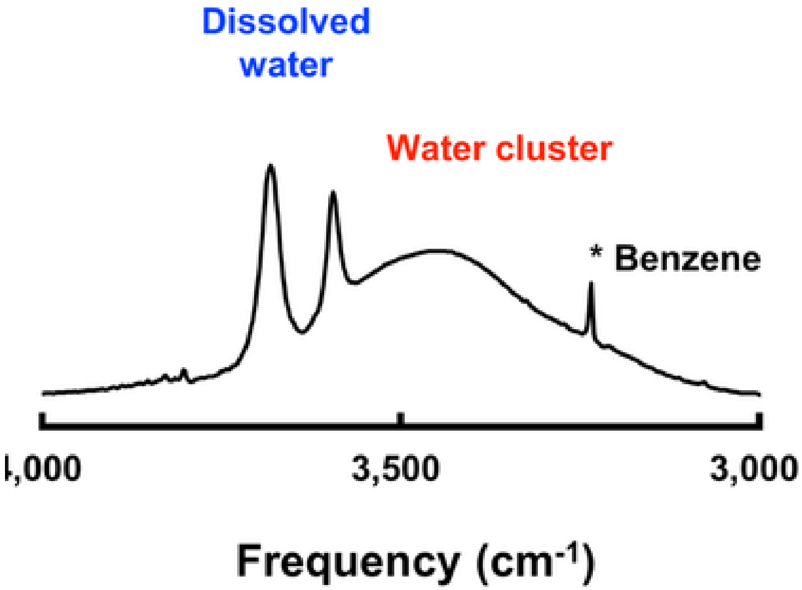
λ = 122.2 mm
f = 2455 MHz

5. Physical Properties

Absorption Spectrum (in the IR range)

- Strong tetrahedrally coordinated hydrogen bonds
  3100 - 3400 cm^{-1}
- Weak hydrogen bonds
  3400 - 3700 cm^{-1}
- Symmetrical valence oscillation
  ν_s = 3594 cm^{-1}
- Asymmetric valence oscillation
  ν_{as} = 3691 cm^{-1}

for highly diluted water in benzene



Lit.: H. Nishide et al., Scientific Reports 9 (2019) 223, DOI: 10.1038/s41598-018-36787-1

5. Physical Properties

Summary

- Water is a substance with a very high specific heat capacity
- It takes more than 5 times the amount of energy to vaporize water than to heat it from 0 to 100 °C.
- It takes more than 6 times the amount of energy to vaporize water than to melt it
- Sublimation, i.e. the direct transition from the solid phase to the gas phase and vice versa, i.e. resublimation, is also important, e.g. in the polar and high mountain regions
- Water has a high thermal conductivity, which can be utilized for effective heat dissipation → Water cooling (active and passive)
- Water is a good solvent for gases, polar liquids and ionic or polar solids
- Due to its polarity, water has a high surface tension
- Water has an optical window in the 200 - 900 nm range and strong IR absorption

6. Hydrogen/Oxygen Chemistry

Hydrogen is the most abundant Element (90%) in the Universe and the primary Fuel for Stellar Energy production (and a Sustainable Energy Economy)

Isotope	Rel. frequency	T_b [°C]	T_m (N_2O) [°C]	T_b(N_2O)
H, H_2	99.985%	-253.5	0.0	100.0
D, D_2	0.015%	-249.2	3.8	101.4
T, T_2	$1 \cdot 10^{-15}$%	-248.0	4.5	101.5

$\downarrow$ **Enrichment during vaporization**

D_2O/H_2O-Relation ⟶ *Climate analysis of ice cores*

- **H_2 has a very low density under standard conditions of 0.0899 g/l (air: 1.30 g/l) ⇒ strong lift ⇒ Balloons / blimps**
- **H_2 has a high specific heat capacity of 14330 J kg^{-1} K^{-1}**
- **H_2 has a high diffusion capacity in many materials**

⇒ Storage in Pd is possible

6. Hydrogen/Oxygen Chemistry

Importance of Hydrogen

1. **Hydrogenation of C=C Bonds ⇒ Hardening of vegetable oils (Margarine)**
   R-CH=CH-R + H_2 → R-CH_2-CH_2-R

2. **Reducing agent ⇒ Synthesis of metals**
   $WO_3 + 3\ H_2 \rightarrow W + 3\ H_2O$

3. **Synthesis of ammonia ⇒ Haber-Bosch Process**
   $N_2 + 3\ H_2 \rightarrow 2\ NH_3$

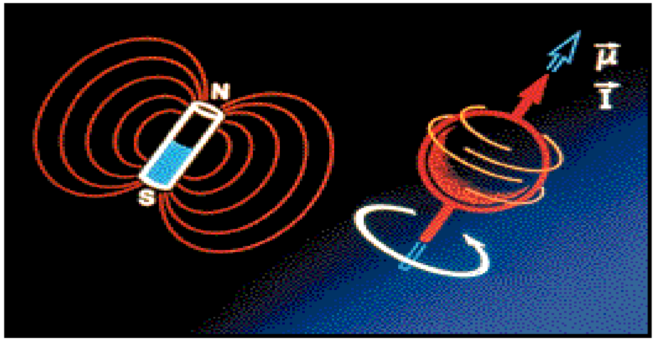
4. **Fuel for spacecraft ⇒ Space Shuttle**

Liquid tank	$2\ H_2 + O_2 \rightarrow 2\ H_2O$
Solid fuel rockets	$8\ Al + 3\ NH_4ClO_4 \rightarrow 4\ Al_2O_3 + 3\ NH_3 + 3\ HCl$
Steering gear	$2\ NO_2 + CH_3N_2H_3 \rightarrow 2\ N_2 + CO_2 + 2\ H_2O + H_2$

5. **Energy storage** $2\ H_2O \rightarrow 2\ H_2 + O_2$ ⇒ **Water electrolysis or photolysis**

6. Hydrogen/Oxygen Chemistry

In the ^{1}H-NMR-Spectroscopy (engl.: <u>N</u>uclear <u>M</u>agnetic <u>R</u>esonance) To Elucidate Molecular Structures, Nuclear Magnetic Resonance m_I of the Proton



<u>Principle</u>

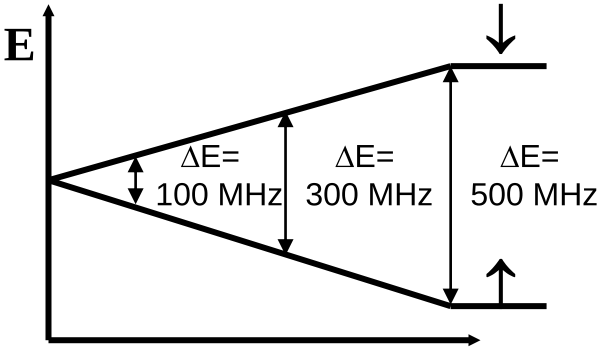
The proton or the ^{1}H-Atomic core has an intrinsic angular momentum (nuclear spin) like the electron

⇒ $P = \sqrt{I(I+1)}\hbar$ with I = 1/2

⇒ 2 Spin states : $m_I = +1/2$ and $m_I = -1/2$

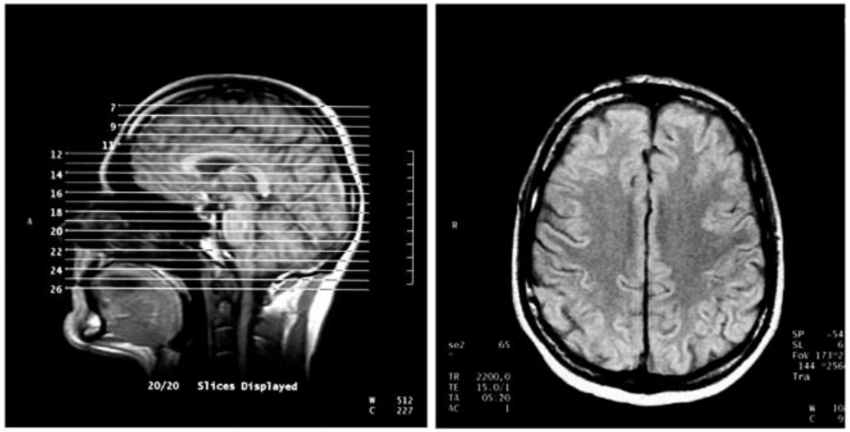
Without magnetic field⇒ Equal energy (degenerate)

Mit Magnetfeld ⇒ Energiedifferenz ΔE



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

Magnetic resonance imaging: Detection of the relaxation time of excited ^{1}H-Cores



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Magnetic field strength B_0 for B_0 = 11.75 Tesla occurs resonance at ν = 500 MHz (Radiowellen)

6. Hydrogen/Oxygen Chemistry

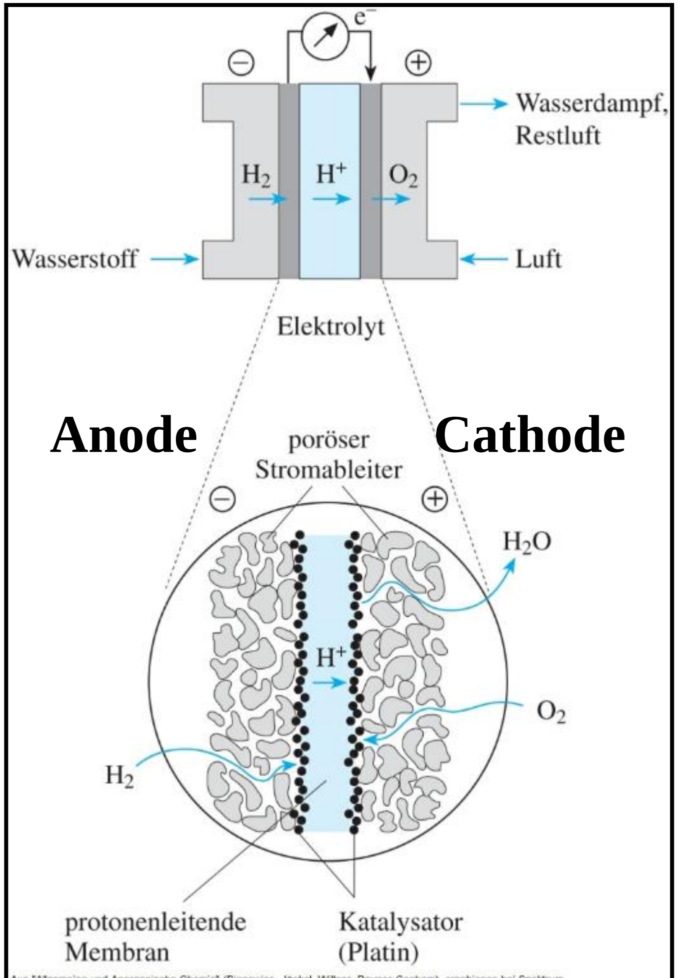
H_2 will become the Key to the Future Energy Supply (as soon as Fossil Fuels become Scarce)

1. Controlled nuclear fusion in magnetic encapsulated plasmas (KFA Jülich, MPI Garching)
   $^2H + {}^3H \rightarrow {}^4He + n$
   ⇒ Centralised power generation

2. Fuel cells
   $2\ H_2 + O_2 \rightarrow 2\ H_2O + 242$ kJ/mol ("Strom")
   Anode: $H_2 + H_2O \rightarrow 2\ H_3O^+ + 2\ e^-$
   Cathode: $1/2\ O_2 + 2\ H_3O^+ + 2\ e^- \rightarrow 3\ H_2O$
   ⇒ Decentralised energy generation + electric vehicles

H_2-Production:	Electrolysis, photolysis
H_2-Transport:	Pipelines, tankers
H_2-Storage:	Liquid tanks, conversion

Construction of a fuel cell



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6. Hydrogen/Oxygen Chemistry

Oxygen (Greek: oxys = engl.: sharp, acid = dt.: scharf, sauer)

Allotropic modifications

Dioxygen O_2

Electro-, photo- or thermolysis of H_2O

Heating precious metal oxides

$2\ HgO \rightarrow Hg + O_2$

$2\ Ag_2O \rightarrow 4\ Ag + O_2$

Decomposition of peroxides

$2\ Na_2O_2 \rightarrow 2\ Na_2O + O_2$

$2\ BaO_2 \rightarrow 2\ BaO + O_2$

Trioxygen (Ozon) O_3

Photolysis of O_2 or sparks in O_2

$O_2 \rightarrow 2\ O\cdot$ $\qquad$ $O_2 + O\cdot \rightarrow O_3$

(Ozoniser, ozone layer: stratosphere)

Photolysis of NO_2 in air

$NO_2 \rightarrow NO + O\cdot$ $\qquad$ $O_2 + O\cdot \rightarrow O_3$

(Summer smog: troposphere)

Reactivity

- **Disoxygen is quite stable and inert at RT : $\Delta H_{diss} = 498$ kJ/mol**
- **Trioxygen is thermodynamically unstable and decomposes when heated slightly or in the presence of catalysts such as MnO_2, PbO_2 according to $2\ O_3 \rightarrow 3\ O_2$**
- **Both O_2 and O_3 are strong oxidising agents**

6. Hydrogen/Oxygen Chemistry

Oxygen and Ozone Dissolve quite well in Water (much better than Hydrocarbons.......)

Solubility of O_2 in H_2O

- **at 25 °C and 1 bar ~ 40 mg per liter**
- **Air contains 20.95% O_2 ⇒ ~ 8 mg per liter**
- **Solubility decreases with increasing temperature**
  ⇒ Cold waters are rich in fish (Humboldt Current)
- **Oxygen-free chemistry in solution requires thorough rinsing with an inert gas (Ar, N_2)**

Toxicity of O_2 and O_3

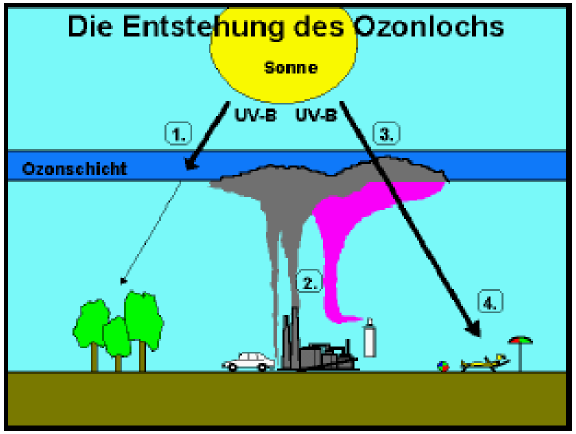
< 8% O_2 ⇒ Suffocation due to lack of oxygen

> 60% O_2 ⇒ Formation of harmful hyperoxide O_2^-

O_3 is extremely toxic : MAK value = 0.2 mg/cm^3 ~ 0.1 ppm (parts per million)

6. Hydrogen/Oxygen Chemistry

As a Result of the Biogenic Formation of O_2, the Ozone layer was also created by the Photolysis of O_2



Stratosphere (15 - 50 km)

$$O_2 \xrightarrow[< 240\ nm]{h\nu} 2\ O\cdot \qquad\qquad O_2 + O\cdot \underset{< 310\ nm}{\overset{h\nu}{\rightleftharpoons}} O_3$$

(UV-C and VUV) *(UV-B and UV-C)*

$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$ $NO\cdot + O_3 \rightarrow NO_2\cdot + O_2$

$ClO\cdot + O \rightarrow Cl\cdot + O_2$ $NO_2\cdot + O \rightarrow NO\cdot + O_2$

$Cl\cdot$ comes from the FCHC = Fluorochlorohydrocarbons

z.B. $CFCl_3$, CF_2Cl_2 $C_xF_yCl_z \rightarrow C_xF_yCl_{z-1}\cdot + Cl\cdot$

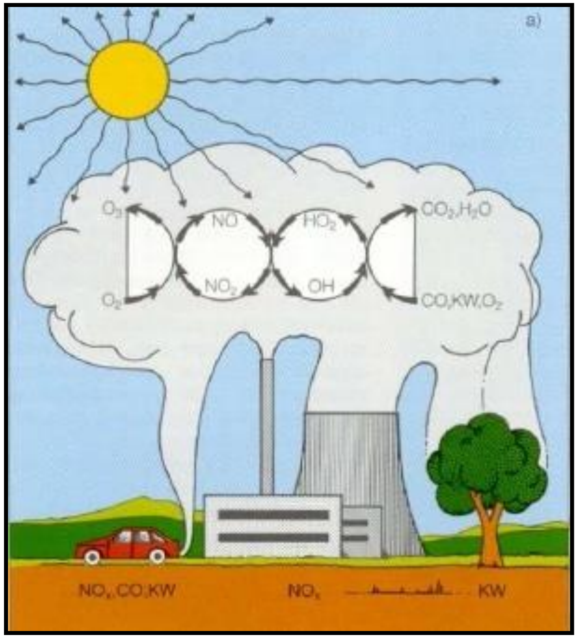
Troposphere (0 – 10 km)

Exhaust gases: $CO, C_xH_y + O_2 \rightarrow CO_2 + H_2O$

$2\ NO + O_2 \rightarrow 2\ NO_2$

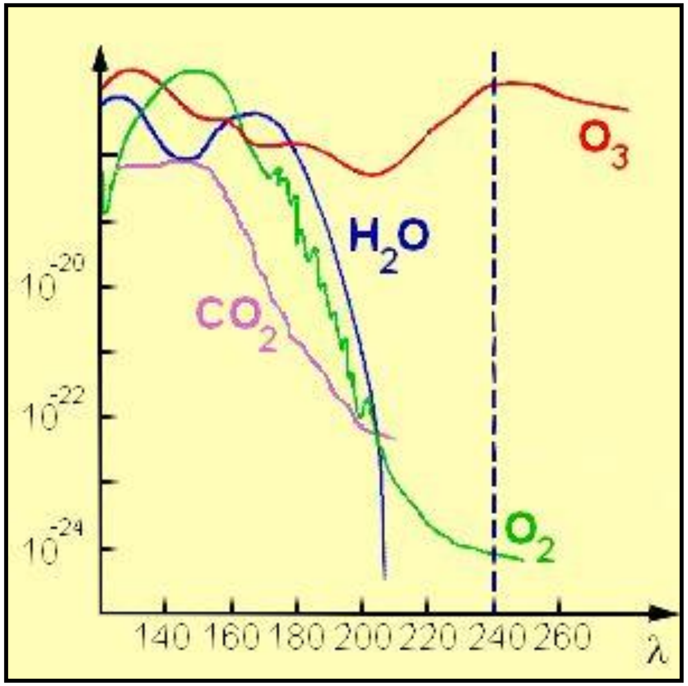
$NO_2 + O_2 \rightarrow NO + O_3$

(Summer smog : $O_3 > 180\ \mu g/m^3$ air)



6. Hydrogen/Oxygen Chemistry

Photochemistry of the Atmosphere



Selected photodissociation reactions

$N_2 + h\nu(< 120\ nm) \rightarrow 2\ N\cdot$

$CH_4 + h\nu(< 160\ nm) \rightarrow {}^1CH_2 + H_2$

$H_2O + h\nu(< 200\ nm) \rightarrow H\cdot + OH\cdot$

$2\ O_2 + h\nu(< 200\ nm) \rightarrow 2\ O\cdot$

$CO_2 + h\nu(< 200\ nm) \rightarrow CO + O\cdot$

$O_3 + h\nu(< 320\ nm) \rightarrow {}^1O_2 + {}^1O$

$HNO_3 + h\nu(< 320\ nm) \rightarrow NO_2 + OH\cdot$

$NO_2 + h\nu(< 410\ nm) \rightarrow NO + O\cdot$

$Cl_2 + h\nu(< 450\ nm) \rightarrow 2\ Cl\cdot$

Formation of the OH radical (atmospheric detergent)

$NO_2 + h\nu(< 410\ nm) \rightarrow NO + O\cdot$

$O\cdot + H_2O \rightarrow 2\ OH\cdot$

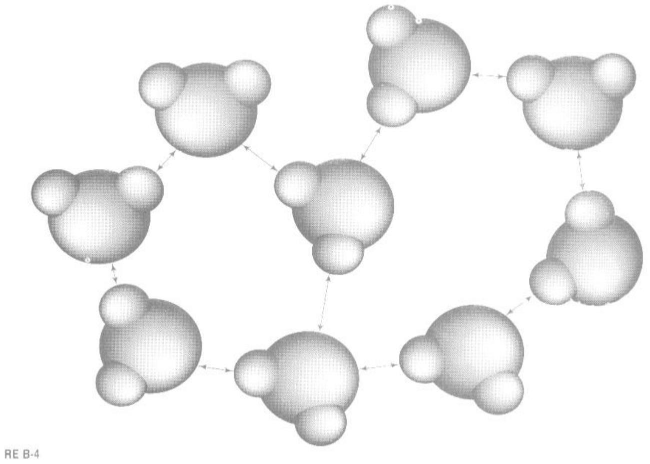
Side reactions : $2\ O_2 + 2\ O\cdot \rightarrow 2\ O_3$ $O_3 + H_2O \rightarrow O_2 + H_2O_2$ $2\ H_2O_2 \rightarrow 2\ H_2O + {}^1O_2$

Radicals in the atmosphere : $OH\cdot$, $NO\cdot$, $HOO\cdot$, $O\cdot$, $R\text{-}CH_2\cdot$, $NO_3\cdot$

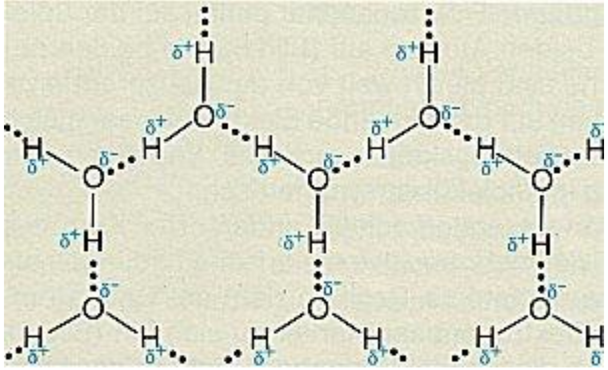
6. Hydrogen/Oxygen Chemistry

Water H_2O

- Detection and determination
- Structure
- Solvent properties
- Activity
- Autoprotolysis
- pH value
- Medium for electrolytes



Liquid water (hydrogen bonding)



Solid water (hydrogen bonding)

6. Hydrogen/Oxygen Chemistry

Water - Qualitative Detection

Anhydrous, white copper sulphate $CuSO_4$ turns blue in the presence of water

⇒ Four H_2O molecules coordinate square-planar at the Cu^{2+}, a fifth is bound to the sulphate anions via H-bridges

$$[Cu(H_2O)_4]SO_4\cdot H_2O \xrightarrow[-2H_2O]{100°C} CuSO_4\cdot 3H_2O \xrightarrow[-2H_2O]{130°C} CuSO_4\cdot H_2O \xrightarrow[-H_2O]{250°C} CuSO_4$$

Water - Quantitative determination

Karl-Fischer-Titration

(Amperometry in anhydrous medium)

$$I_2 + SO_2 + 2\ H_2O \rightarrow SO_4^{2-} + 2\ I^- + 4\ H^+$$

6. Hydrogen/Oxygen Chemistry

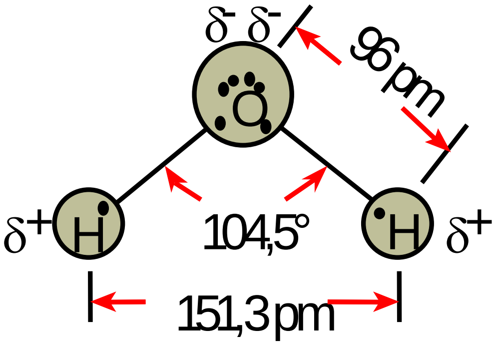
Water Structure: The Special Properties of Water can be Traced back to the Structure of the H_2O Molecule and the Strongly Differing Electronegativity of the Return Binding Partner

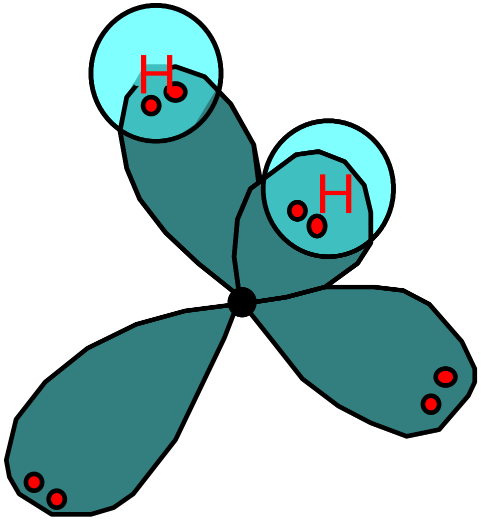
1. Strongly polarised O-H atomic bonds lead to to a molecule with a high dipole moment
   ⇒ $\mu = q \cdot d = 1.85$ Debye ⇒ High polarity and strong hydrogen bonds

2. Formal hybridisation of the orbitals of the oxygen-atoms to four equivalent hybrid orbitals
   $2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1 \rightarrow 4 \times 2sp^3$ (Tetraeder: 109° 28')

$2 \times sp^3$	Bonding to hydrogen
$2 \times sp^3$	No bonds

⇒ Angled structure with low Deviation from the tetrahedral angle

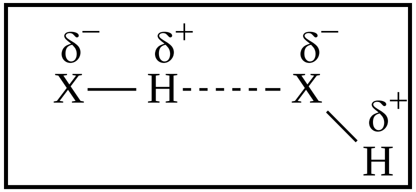


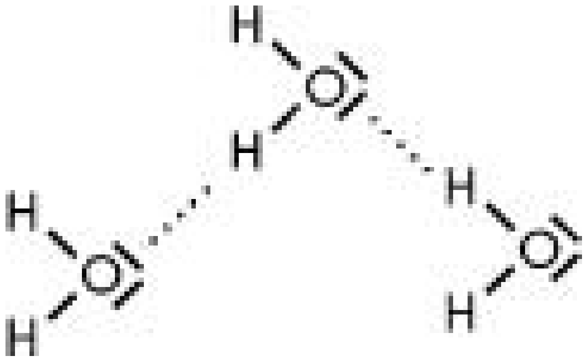


6. Hydrogen/Oxygen Chemistry

Water Structure: H-bridge Bond between HX Molecules (X = N, P, O, S, F, Cl)

Between the positively charged H atom of the molecule HX and the free electron pair of an X atom of a neighbouring molecule results in an electrostatic attraction



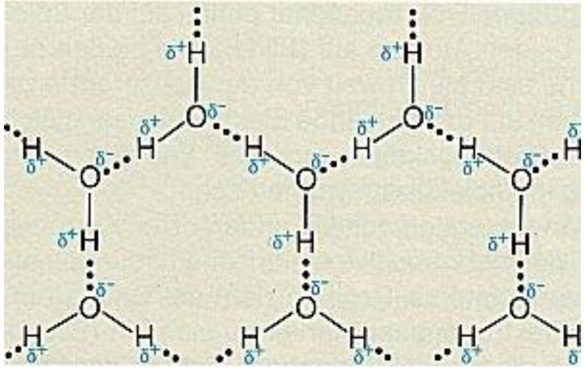


X = F, O, N ⇒ Strong hydrogen bonds
X = Cl, S, P ⇒ Weak hydrogen bonds

The hydrogen bonds X─H····X are usually arranged linearly, as the attraction is then H····X the greatest or the repulsion between the X atoms is the smallest.

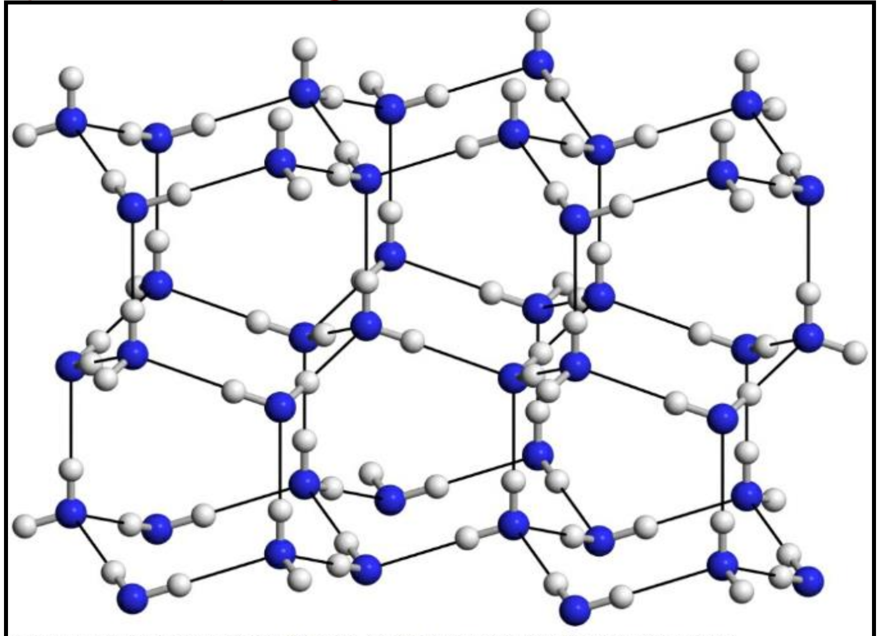
Liquid water ⇒ Each H_2O-molecule is characterized by three to four neighboring molecules via hydrogen bonds

Solid water (ice) ⇒ Each H_2O molecule is linked to four neighboring molecules via hydrogen bonds

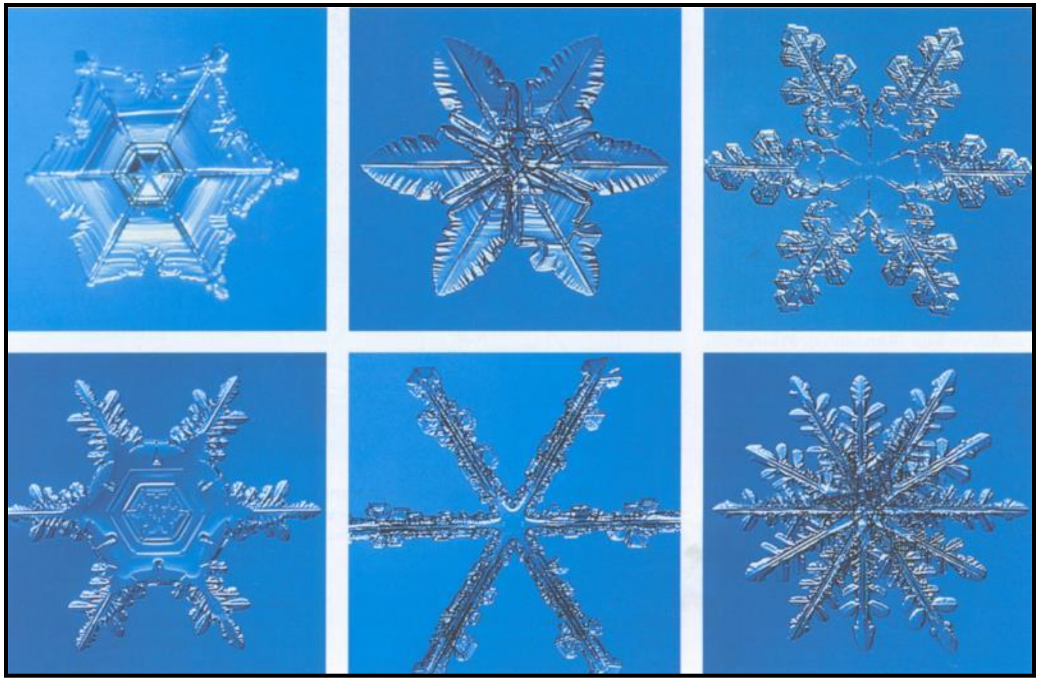


6. Hydrogen/Oxygen Chemistry

Water Structure: In ice, each Oxygen Atom is Tetrahedrally Surrounded by four Hydrogen Atoms



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung14-13.jpg



Temperature [°C]	Density [g/ml]	
0 (Ice)	0.9168	⇒ Open, hexagonal structure with cavities
0 (Water)	0.99984	⇒ Decrease in volume during melting!
4	1.000000	⇒ Density anomaly of water
10	0.99970	⇒ Thermal volume increase from 4 °C
20	0.99821	

6. Hydrogen/Oxygen Chemistry

Water - Solution properties: Polar substances, i.e. molecular compounds such as e.g. sugar, or ionic compounds, such as salts, are not converted into a liquid due to the polar Character easily solved

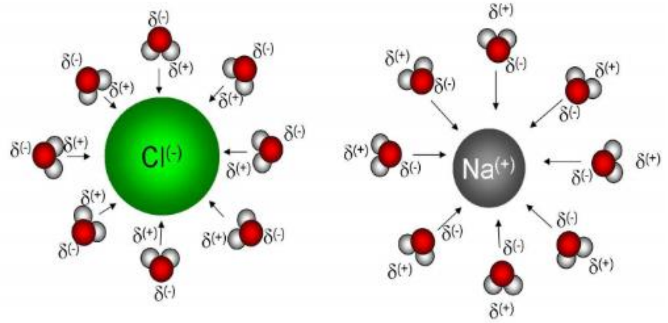


Abb.: Hydratation von Kationen und Anionen in Wasser

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$ $\quad\quad$ $\Delta H_L = - 787$ kJ/mol

Dissolved ions are always hydrated in water (aq)

⇒ Depending on their ionic charge density, they are typically characterized by four to six H_2O molecules (coordinated)

⇒ Water reduces the strength of electrostatic interactions with the state in a vacuum, by a factor of 80 (dielectric constant $\varepsilon_r = 80$)

The hydration of salts can be exothermic or endothermic:

$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2\ Cl^-(aq)$ $\quad\quad$ $\Delta H_L = - 81$ kJ/mol

$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$ $\quad\quad$ $\Delta H_L = + 15$ kJ/mol ⇒ Cooling mixtures

6. Hydrogen/Oxygen Chemistry

Water - Solution Properties: Ionic Compounds (e.g. Salts)

$A_mB_n(s) \rightleftharpoons m\,A^{n+}(aq) + n\,B^{m-}(aq)$

For the salt A_mB_n the equilibrium constant K is given by:

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

Since the concentration of A_mB_n is constant at constant temperature, the equation can also be multiplied by $c(A_mB_n) \Rightarrow$ Solubility product K_L

i.e. $K_L = K\cdot c(A_nB_m)$ with the unit $[mol^{(m+n)}l^{-(m+n)}]$ results in:

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

<u>Example: $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$</u>

$K_L = c(Ag^+)\cdot c(Cl^-) = 2\cdot10^{-10}\ mol^2/l^2$

$pK_L = 9.7$ mit $p = -\log_{10} \Rightarrow$ „Operator“

Concentration of Ag^+-ions: $c(Ag^+) = \sqrt{K_L} = 1.4\cdot10^{-5}$ mol/l, because $c(Ag^+) = c(Cl^-)$

6. Hydrogen/Oxygen Chemistry

Water - Solubility Products of sparingly Soluble Ionic Compounds in H_2O at 25 °C

Salt	pK_L-Value	Salt	pK_L-Value	Salt	pK_L-Value
LiF	2.8	SnS	27.5	$MgCO_3$	7.5
MgF_2	8.2	PbS	52.7	$CaCO_3$	8.4
CaF_2	10.4	MnS	36.1	$SrCO_3$	9.0
BaF_2	5.8	NiS	19.4	$BaCO_3$	8.3
PbF_2	7.4	FeS	18.1	$PbCO_3$	13.1
$PbCl_2$	4.8	CuS	36.1	$ZnCO_3$	10.0
PbI_2	8.1	Ag_2S	59.1	$CdCO_3$	13.7
CuCl	7.4	ZnS	24.7	Ag_2CO_3	11.2
CuBr	8.3	CdS	27.0	$SrCrO_4$	4.4
CuI	12.0	HgS	52.7	$BaCrO_4$	9.7
AgCl	9.7	Bi_2S_3	71.6	$PbCrO_4$	13.8
AgBr	12.3	$CaSO_4$	4.6	Ag_2CrO_4	11.9
AgI	16.1	$SrSO_4$	6.5	$Sc(OH)_3$	30.7
Hg_2Cl_2	17.9	$BaSO_4$	10.0	$Al(OH)_3$	32.3
Hg_2I_2	28.3	$PbSO_4$	7.8	$Fe(OH)_3$	38.8

6. Hydrogen/Oxygen Chemistry

Water - Rules for the Solubility of Ionic Compounds

- **The solubility is temperature-dependent (and pressure-dependent)**
- **The solubility increases with the increase in hydration of the ions and decreases with the increase in lattice energy**
- **Easily soluble:** **Alkali metal salts, magnesium salts**
  All! Nitrates (nitrate problem), halides, (sulphates)
  ⇒ Surface water
- **Poorly soluble:** **Heavy metal salts (Sr, Ba, Pb, Co, Ni, Cu, Zn, Cd, Hg, …)**
  Aluminates, carbonates, phosphates, silicates, sulphides
  ⇒ Earth's crust
- **Solubility of the hydroxides:**

$$NaOH > Mg(OH)_2 > Al(OH)_3 > Fe(OH)_3 > Si(OH)_4$$

⇒ Cause: Increase in ion charge density (electric field strength) = Ion charge/ion radius

6. Hydrogen/Oxygen Chemistry

Water - Characteristic Ion Concentrations in Natural Water (in mol/l)

Ion	Sea water	Fresh water	Rain water	Fog drops
H^+	$1 \cdot 10^{-8}$	$2 \cdot 10^{-8}$	$1 \cdot 10^{-4}$	$2 \cdot 10^{-3}$
Mg^{2+}	$5 \cdot 10^{-2}$	$4 \cdot 10^{-4}$	$4 \cdot 10^{-6}$	$8 \cdot 10^{-5}$
Na^+	0.48	$5 \cdot 10^{-4}$	$2 \cdot 10^{-6}$	$3 \cdot 10^{-4}$
Ca^{2+}	$1 \cdot 10^{-2}$	$1 \cdot 10^{-3}$	$5 \cdot 10^{-7}$	$2 \cdot 10^{-4}$
Cl^-	0.56	$3 \cdot 10^{-4}$	$2 \cdot 10^{-5}$	$2 \cdot 10^{-4}$
SO_4^{2-}	$3 \cdot 10^{-2}$	$2 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	$3 \cdot 10^{-4}$
NO_3^-	$3 \cdot 10^{-5}$	$6 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-3}$

Trend in the frequency of cations: $Na^+ > Mg^{2+} > Ca^{2+}$

Trend in the frequency of anions: $Cl^- > SO_4^{2-} \sim NO_3^-$

6. Hydrogen/Oxygen Chemistry

Water - Activity and Activity-Coefficient

Experimental studies on the solubility of salts show that the solubility depends on the concentration of the salt depends on the concentration of the salt and that of foreign salts

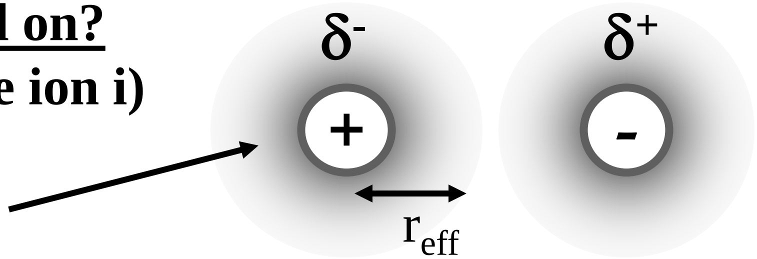
Activity: $a = \gamma \cdot c$ (Effective or efficient concentration)

Size of the activity coefficient γ

Highly diluted solutions	$\gamma \approx 1.0$	**i.e. $a = c$**
Concentrated solutions	$\gamma = 0.0 \ldots 1.0$	**i.e. $a < c$**

What does the size of the activity coefficient depend on?

- **Ionic strength $I = 0.5\Sigma c_i \cdot z_i^2$ (z_i = Ion charge of the ion i)**
- **Effective ionicradius r_{eff}: Ion + Hydrationshell (The hydrate shell weakens the attractive interaction)**



6. Hydrogen/Oxygen Chemistry

Water - Activity Coefficient of selected Ions in H_2O at 25 °C

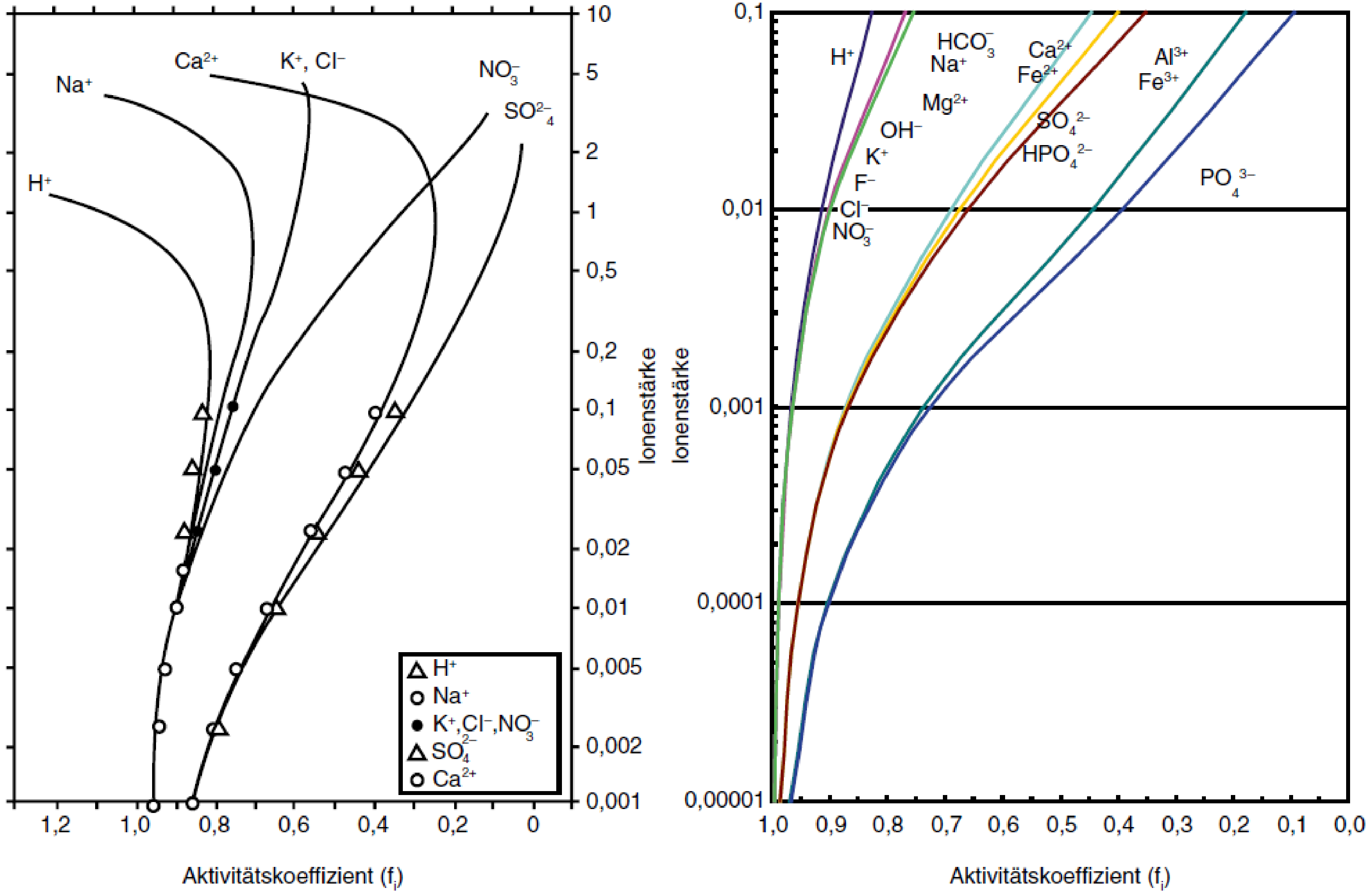
		Activity coefficient for ionic strength I [mol/l]		
Ion	r_{eff} [pm]	I = 0.001	I = 0.01	I = 0,1
H^+	900	0.967	0.914	0.830
Li^+	600	0.965	0.907	0.810
Na^+, HCO_3^-, HSO_4^-, $H_2PO_4^-$	400	0.964	0.901	0.770
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300	0.964	0.899	0.755
Mg^{2+}, Be^{2+}	800	0.872	0.690	0.450
Ca^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}	600	0.870	0.675	0.405
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, WO_4^{2-}	500	0.868	0.670	0.380
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, CrO_4^{2-}, HPO_4^{2-}	400	0.867	0.660	0.355
Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, La^{3+}	900	0.738	0.445	0.180
PO_4^{3-}, $[Fe(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$	400	0.725	0.395	0.095

Calculation of the activity coefficients according to Debye and Hückel

$$\boxed{\log \gamma = \frac{-0.51 \cdot z \cdot \sqrt{I}}{1 + (r_{eff} \sqrt{I}/305)}}$$

6. Hydrogen/Oxygen Chemistry

Water - Activity Coefficients of Selected Ions in H_2O at 25 °C

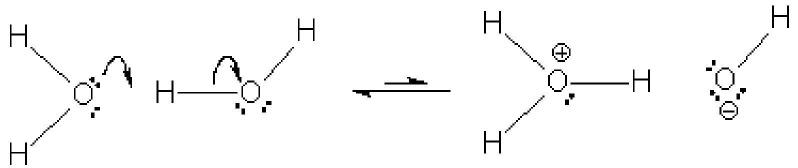


Data according to Garels and Christ 1965 (left) and according to Hem 1989 (right)

6. Hydrogen/Oxygen Chemistry

Autoprotolysis of Water: The Molecule Dissociates into H^+ and OH^- and can Occur both as an Acid and as a Base

Even the purest water contains OH^- and H_3O^+ ions, resulting in a low but still measurable electrical conductivity



$$2\ H_2O \rightleftharpoons H_3O^+ + HO^-$$

$$\boxed{K \quad = \quad \frac{[H^+]\cdot[OH^-]}{[H_2O]} \quad = \quad 10^{-14}}$$

Since the water concentration is constant at 55.5 mol/l $[H_2O]$ can be drawn into the constant:

$$K_W = K[H_2O] = [H_3O^+][OH^-]\ (mol^2/l^2)$$

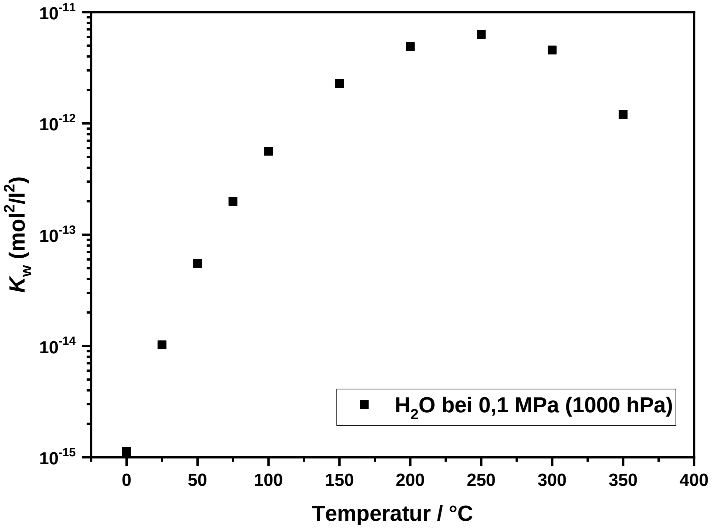
Temperature dependence of the ion product of water

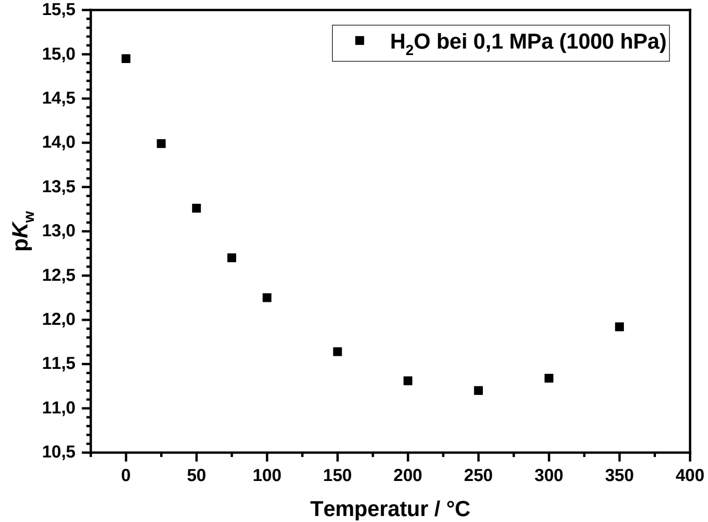
T [°C]	K_W [mol²l⁻²]	pK_W
0	$0.114\cdot10^{-14}$	14.89
10	$0.681\cdot10^{-14}$	14.16
20	$0.929\cdot10^{-14}$	14.03
25	$1.008\cdot10^{-14}$	14.00
30	$1.469\cdot10^{-14}$	13.83
40	$2.919\cdot10^{-14}$	13.53
50	$5.474\cdot10^{-14}$	13.26
100	$134.9\cdot10^{-14}$	12.13

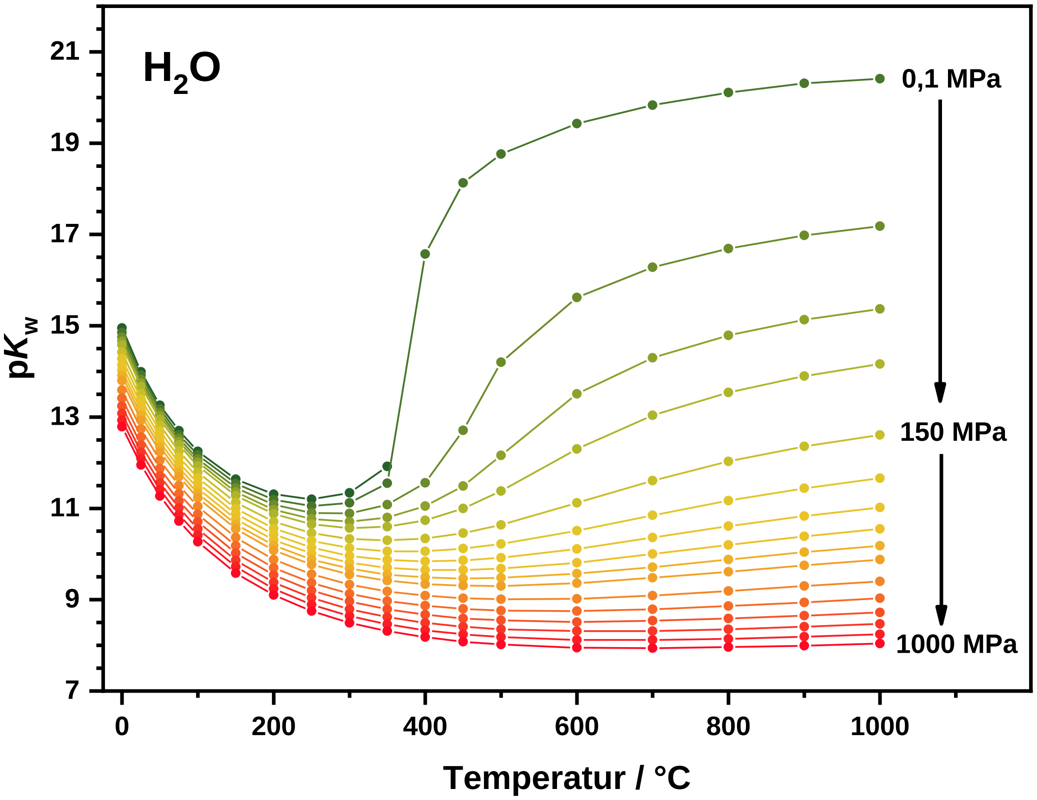
This equilibrium constant is called the ionic product of water, which at 22 °C is exactly $1.0\cdot10^{-14}$ mol²/l²

6. Hydrogen/Oxygen Chemistry

Autoprotolysis of Water: Temperature and Pressure dependence







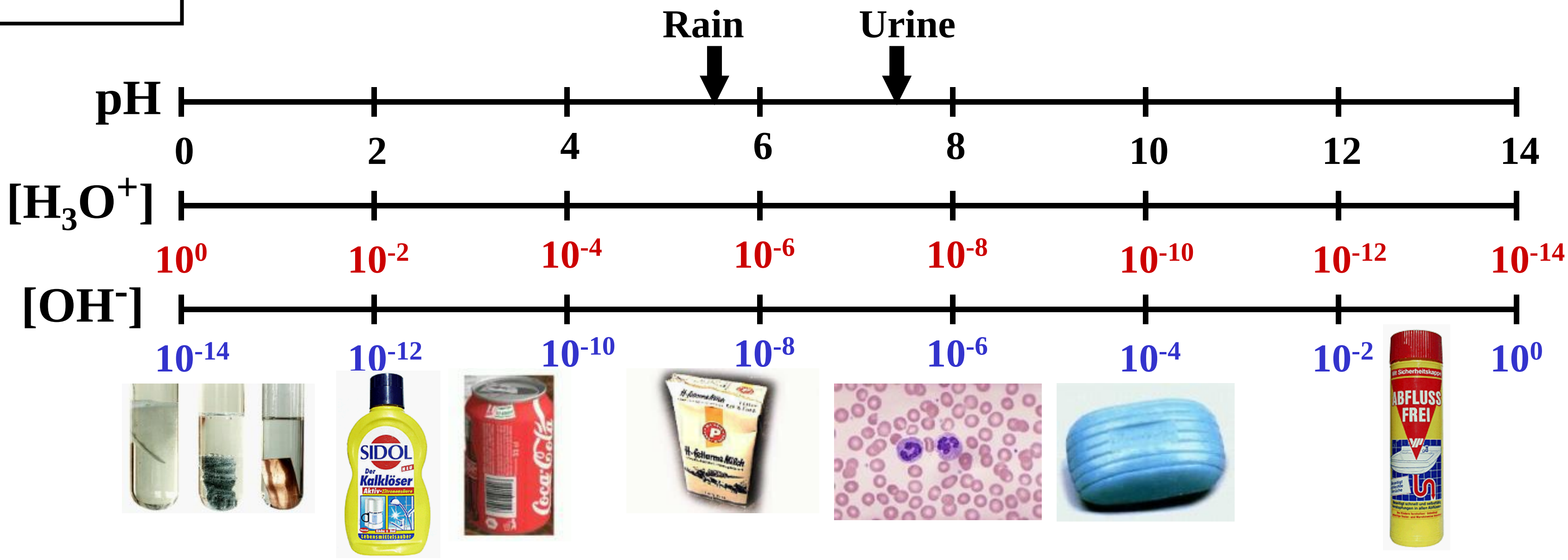
Lit.: The Ionization Constant of Water over Wide Ranges of Temperature and Density, Andrei V. Bandura, Sergei N. Lvov, Journal of Physical and Chemical Reference Data 35, 15 (2006)

6. Hydrogen/Oxygen Chemistry

Water - The pH value (lat.: potentia Hydrogenii)

$\boxed{pH = -\log[H_3O^+]}$ negative decadic logarithm of the hydrogen ion concentration

$\boxed{pOH = -\log[OH^-]}$ negative decadic logarithm of the hydroxide ion concentration


Rain

Urine

pH: 0, 2, 4, 6, 8, 10, 12, 14

$[H_3O^+]$: 10^0, 10^{-2}, 10^{-4}, 10^{-6}, 10^{-8}, 10^{-10}, 10^{-12}, 10^{-14}

$[OH^-]$: 10^{-14}, 10^{-12}, 10^{-10}, 10^{-8}, 10^{-6}, 10^{-4}, 10^{-2}, 10^0

- In aqueous solutions, the product of the concentration of H_3O^+- and OH^--Ions s always is always constant: $pH + pOH = pK_W$
- The pH value may be slightly off the usual scale pH = -1 $\Rightarrow$ $[H^+] = 10$ mol/l

6. Hydrogen/Oxygen Chemistry

Water - pH Value Calculation for Acids

Acidity	$c(H_3O^+)$	pH value
Very strong **$pK_A < -1.74$**	$\boxed{c(H_3O^+) = c_0(HA) + 10^{-7}}$	$\boxed{pH = -\log\left(c_0(HA) + 10^{-7}\right)}$
Strong **$-1.74 < pK_A < 4.5$**	$\boxed{c(H_3O^+) = -\frac{K_S}{2} + \sqrt{\frac{K_S{}^2}{4} + K_S \cdot c_0(HA)}}$	$\boxed{pH = -\log\left(-\frac{K_S}{2} + \sqrt{\frac{K_S^2}{4} + K_S \cdot c_0(HA)}\right)}$
Medium strong **$4.5 < pK_A < 9.5$**	$\boxed{c(H_3O^+) = \sqrt{K_S \cdot c_0(HA)}}$	$\boxed{pH = \frac{1}{2}\left(pK_S - \log\left(c_0(HA)\right)\right)}$
(Very) weak **$pK_A > 9.5$**	$\boxed{c(H_3O^+) = \sqrt{K_S \cdot c_0(HA) + K_W}}$	$\boxed{pH = -\frac{1}{2} \cdot \log\left(K_S \cdot c_0(HA) + K_W\right)}$

6. Hydrogen/Oxygen Chemistry

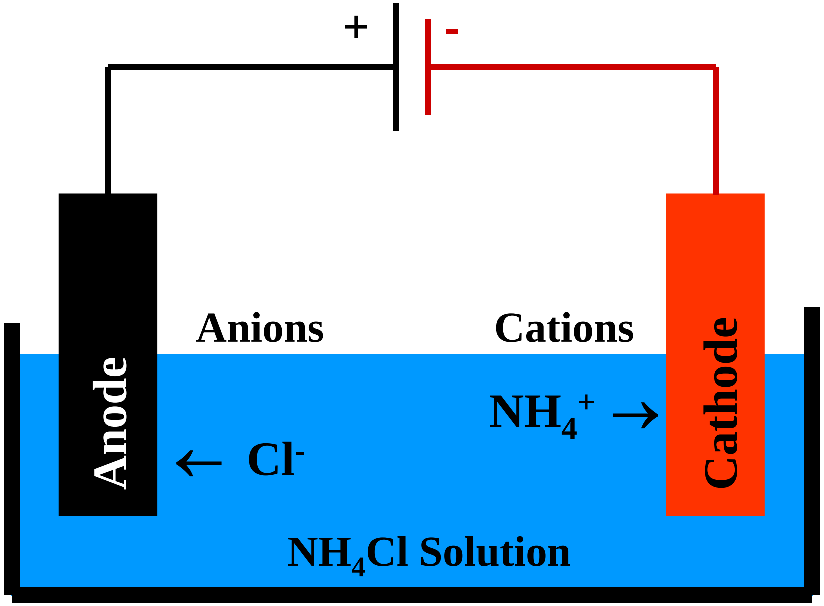
Water - Electrolytes: Compounds that dissolve in Water to form freely Mobile Ions

1. **Ionic compounds**

   $NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$

2. **Strong polar covalent compounds**

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



⇒ **Formation of freely mobile ions**

⇒ **Facilitated current transport or increase in electrical conductivity**

In contrast, substances such as sugar or alcohol, whose aqueous solutions do not conduct electricity are referred to as non-electrolytes

6. Hydrogen/Oxygen Chemistry

Water - Electrolytes: Conductivity of Aqueous Solutions of Various Compounds

$$\boxed{\kappa = \frac{1}{R} \cdot \frac{l}{q} [\mu S / cm]}$$

with R = Electrical resistance, q = Plate distance

Solution	c [mol/l]	κ	Explanation
Distilled water	**55.5**	**13**	**Autoprotolysis of H_2O and dissolved CO_2** $2\ H_2O \rightleftharpoons H_3O^+ + OH^-$ $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H_3O^+$
NaCl-Solution	**0.1**	**10,620**	**Strong electrolyte**
D-Glucose-Solution	**0.1**	**14**	**Non electrolyte (Autoprotolysis of H_2O + dissolved CO_2)**
HCl	**0.01**	**24,300**	**Strong electrolyte and high ion mobility**
CH_3COOH	**0.1**	**522**	**Weak electrolyte**

6. Hydrogen/Oxygen Chemistry

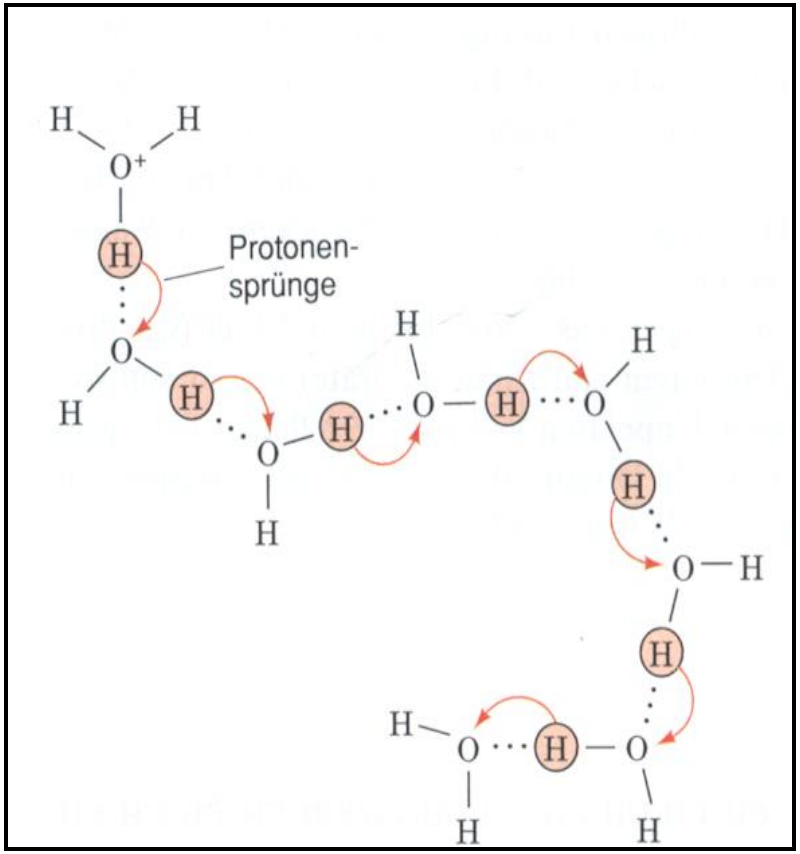
Water - Electrolytes: Ion Mobility in Aqueous Solutions at 298 K

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

The high proton conductivity is crucial for many bio-chemical processes

⇒ e.g. for transmembrane proton pumps

Proton jump mechanism for Hydronium ions in aqueous solutions



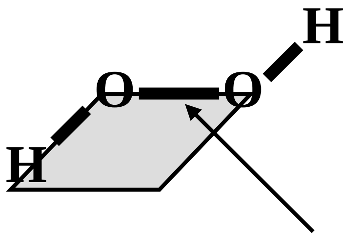
6. Hydrogen/Oxygen Chemistry

Hydrogen Peroxide H_2O_2 is a slightly bluish Liquid with a high Viscosity

Structure

Two OH-units, that are at an angle, the dieder angle, of 111° to each other

$Na_2CO_3 \cdot H_2O_2 \rightarrow Na_2CO_3 + H_2O_2 \rightarrow 2\,OH^{\cdot}$



Relatively weak O-O bond as a predetermined breaking point → $2\,OH^{\cdot}$ radicals

Reactivity

- H_2O_2 is thermodynamically unstable

  $2\,H_2O_2(l) \rightarrow 2\,H_2O(l) + O_2(g) \quad \Delta G_R = -117$ kJ/mol
- Stabilizers are often added to commercially available solutions of 30 - 35% H_2O_2 in H_2O to slow down decomposition
- The decomposition is catalyzed by metals, dust, blood, light, metal oxides, etc.
- Strong oxidizing agent
- The peroxide anion O_2^{2-} is a very strong base:

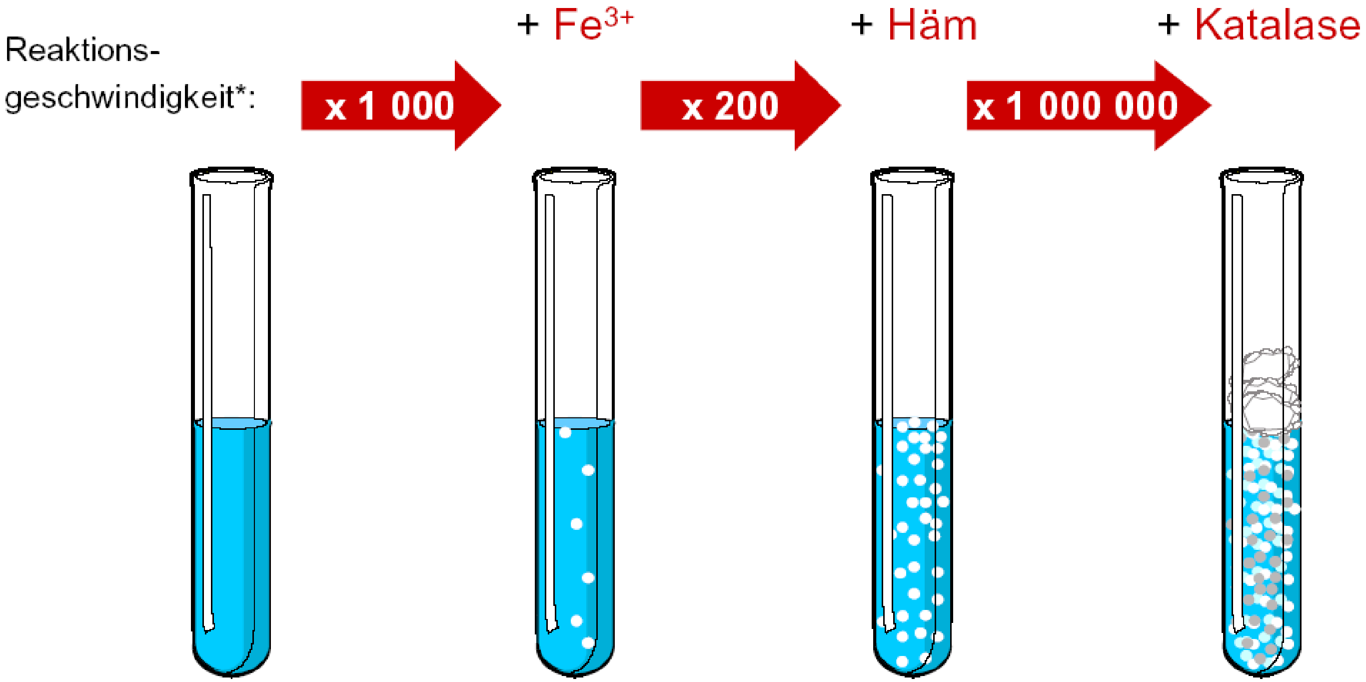
  $Na_2O_2(s) + 2\,H_2O(l) \rightarrow 2\,NaOH(aq) + H_2O_2(aq)$

6. Hydrogen/Oxygen Chemistry

Hydrogen Peroxide H_2O_2 - Decomposition

$2\ H_2O_2 \rightarrow 2\ H_2O + {}^1O_2$

Catalysts: $Mn^{3+/4+}$, $Fe^{2+/3+}$, $Cu^{+/2+}$, Heme, Catalases, …..



*) relative Beschleunigung der Reaktion bei gleicher Katalysator-Konzentration

7. Chemical and Microbiological Contamination

Suspended Solids

Sediments

- **Ground**
- **Layered silicates (talc, clay minerals, mica, kaolin, ...)**
- **Other insoluble minerals**

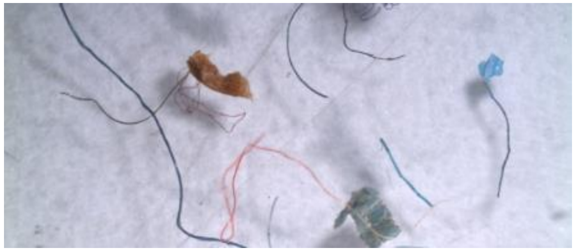
Organic solids

- **Plant residues**
- **Animal remains**
- **Microorganisms**
- **(Micro) plastics**

7. Chemical and Microbiological Contamination

Suspended Solids: Microplastics and their Morphology

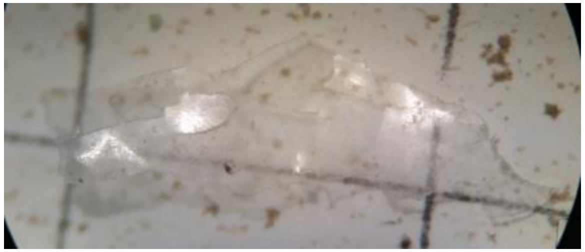
Fibres



Pellets

Primary microplastics
Plastic particles that enter the marine environment on a microscale

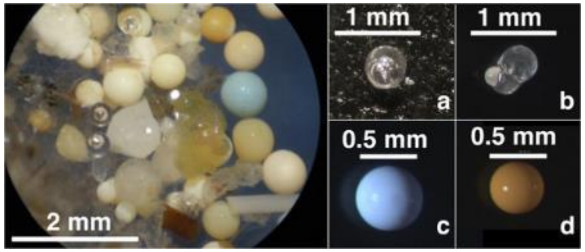
Films



Fragments

Foam

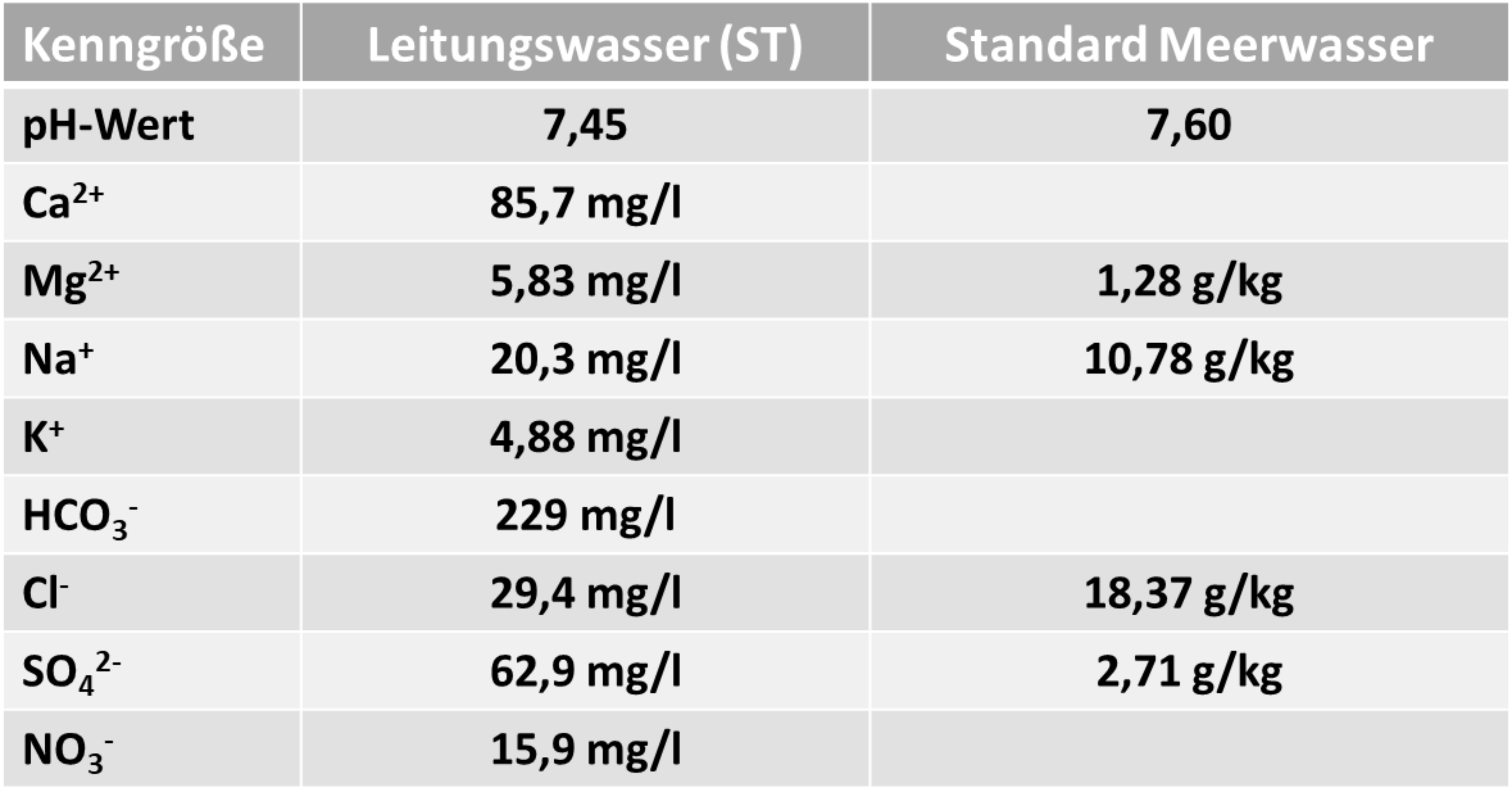
Microbeads



Secondary microplastics
Formed by abrasion from larger plastic parts that end up in the marine environment

7. Chemical and Microbiological Contamination

Dissolved Ions - Salts



Kenngröße	Leitungswasser (ST)	Standard Meerwasser
pH-Wert	7,45	7,60
Ca^{2+}	85,7 mg/l	
Mg^{2+}	5,83 mg/l	1,28 g/kg
Na^{+}	20,3 mg/l	10,78 g/kg
K^{+}	4,88 mg/l	
HCO_3^-	229 mg/l	
Cl^-	29,4 mg/l	18,37 g/kg
SO_4^{2-}	62,9 mg/l	2,71 g/kg
NO_3^-	15,9 mg/l	

Sources: a) F. J. Millero et. al., Deep Sea Research I 55 (2008) 50-72
b) Stadtwerke Steinfurt, www.swst.de

7. Chemical and Microbiological Contamination

Dissolved Ions - Carbonate and Hydrogen-Carbonate "Water Hardness DIN 38409“

$CO_2(g) \rightleftharpoons CO_2(aq)$

$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ „ carbonic acid“ $pK_S(H_2CO_3) = 6.3$

$H_2O(l) + H_2CO_3(aq) \rightleftharpoons H_3O^+ + HCO_3^-(aq) \rightarrow$ pH-value↓ $pK_S(HCO_3^-) = 10.4$

$MCO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons M^{2+}(aq) + HCO_3^-(aq) \rightarrow$ Temporary hardness (M = Mg, Ca)

Temperature increase (scale formation):

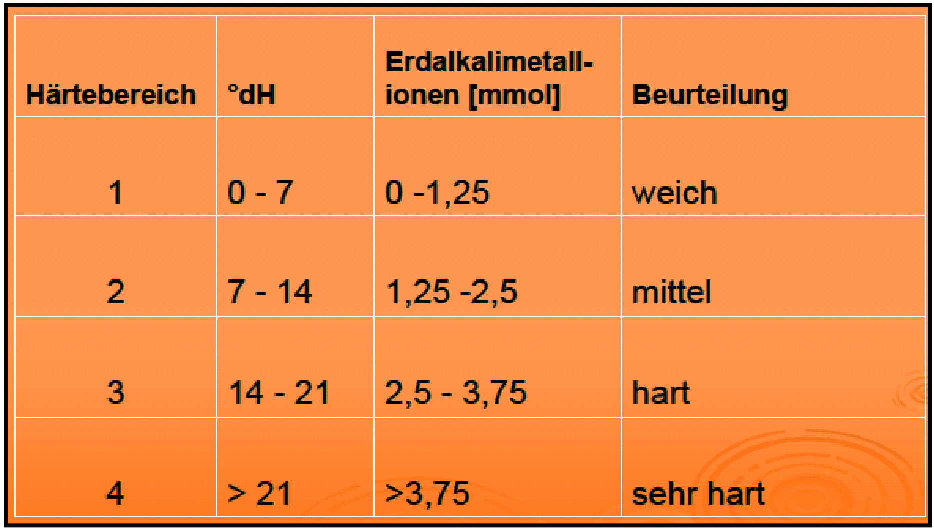
$2\ HCO_3^-(aq) + M^{2+}(aq) \rightarrow$

$MCO_3(s)\downarrow + H_2O(l) + CO_2(s)\uparrow$

Formation of lime soaps

$M^{2+}(aq) + 2\ RCOO^-(aq)$

$\rightarrow M(RCOO)_2(s)\downarrow$



Härtebereich	°dH	Erdalkalimetall-ionen [mmol]	Beurteilung
1	0 - 7	0 -1,25	weich
2	7 - 14	1,25 -2,5	mittel
3	14 - 21	2,5 - 3,75	hart
4	> 21	>3,75	sehr hart

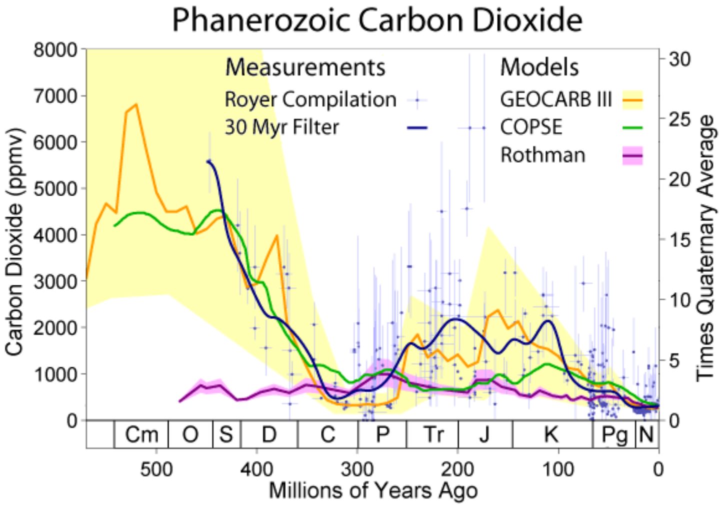
7. Chemical and Microbiological Contamination

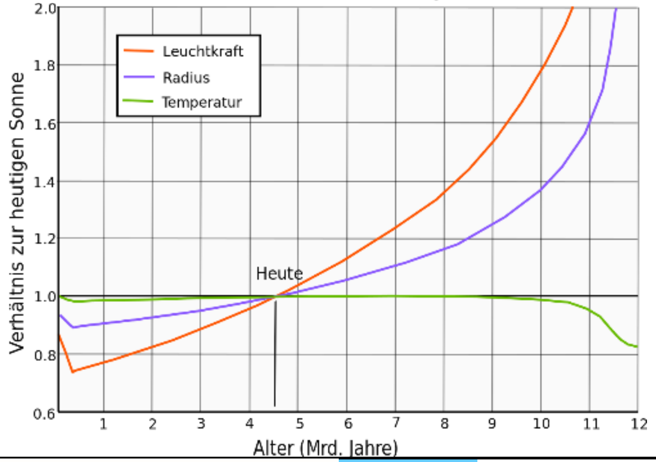
Dissolved Ions - Carbonate and Hydrogen-Carbonate

$CO_2(g) \rightleftharpoons CO_2(aq)$ **Henry constant for CO_2 by 10 °C: 53.077 mol/(m³·bar)**

$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ **„ Carbonic acid“**

CO_2(g) [Vol.-%]	pH(Rainwater)	Year/Epoque
0.0280 (280 ppm)	5.64	1750 (preindustrial)
0.0317	5.62	1960
0.0339	5.60	1980
0.0370	5.58	2000
0.0400	5.57	2015
0.0425 (425 ppm)	5.55	2023
0.2	5.22	Jura
0.7	4.94	Cambrian
1.0	4.87	Precambrian
2.0	4.72	
3.0	4.63	
5.0 (50,000 ppm)	4.52	Archaic



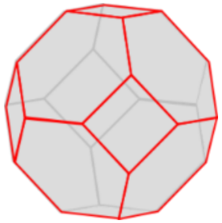


7. Chemical and Microbiological Contamination

Dissolved Ions - Ca^{2+}

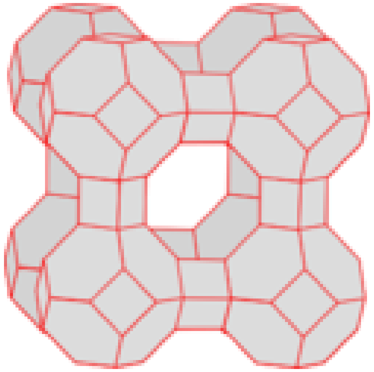
Methods of water softening

1. **Precipitation by boiling: $Ca(HCO_3)_2 \rightleftharpoons CaCO_3(s)\downarrow + H_2O(l) + CO_2(g)\uparrow$**
2. **Precipitation by addition of soda: $Ca(HCO_3)_2 + Na_2CO_3 \rightleftharpoons CaCO_3\downarrow + 2\ NaHCO_3$**
3. **Complexation through phosphates: $Na_5P_3O_{10} + Ca^{2+} \rightleftharpoons CaP_3O_{10}^{3-} + 5\ Na^+$**
4. **Complexing through EDTA: $[H_2EDTA]^{2+} + Ca^{2+} \rightleftharpoons [Ca(EDTA)]^{2+} + 2\ H^+$**
5. **Addition of ion exchangers such as zeolite A**



$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]*27H_2O + Ca^{2+} \rightarrow$$

$$CaNa_{10}[(AlO_2)_{12}(SiO_2)_{12}]*27H_2O + 2\ Na^+$$



Disadvantages of ion exchangers: Formation of poorly degradable sludge

7. Chemical and Microbiological Contamination

Dissolved Ions - Ca^{2+}

Methods of water softening

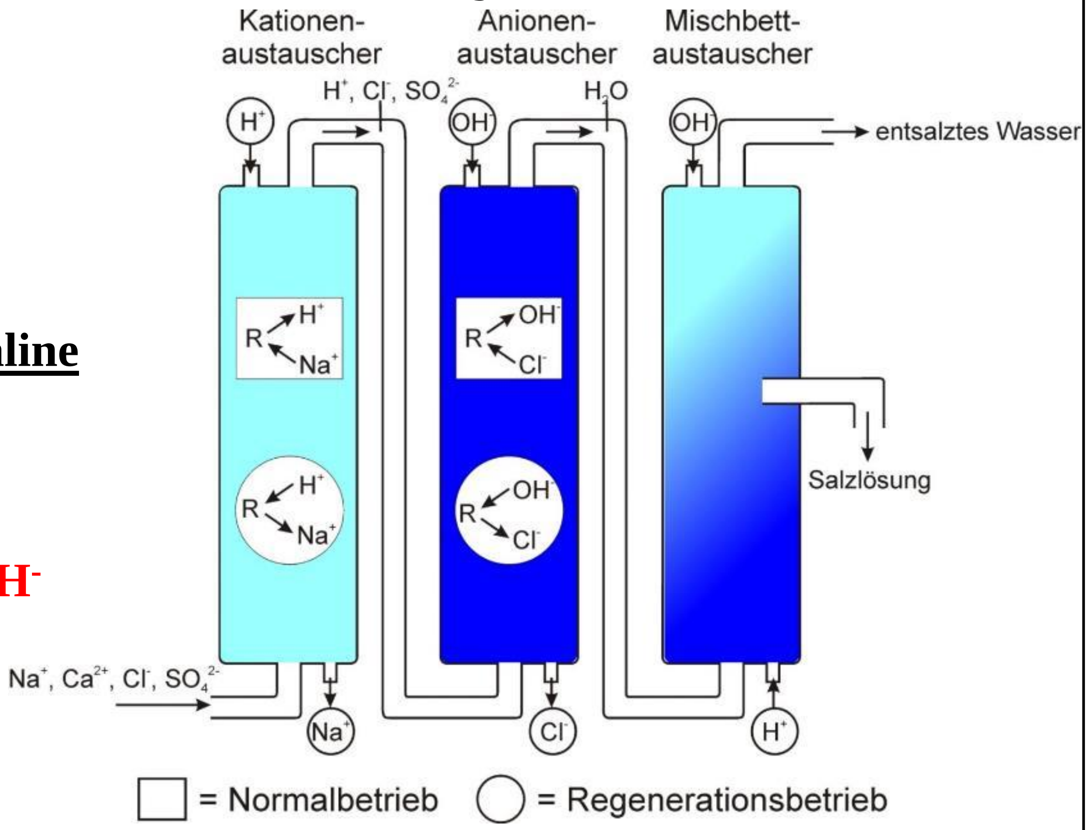
6. Cation exchanger: polymer backbone with acidic groups ($–SO_3H$, $–COOH$)

$2\ R\text{-}SO_3H + Ca^{2+} \rightarrow (R\text{-}SO_3)_2Ca + 2\ H^+$

$H^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < Al^{3+}$

Coupling with anion exchanger with Alkaline Groups ($–N(CH_3)_3OH$, $–NH_2$) leads to demineralisation

$R\text{-}N(CH_3)_3OH + Cl^- \rightarrow R\text{-}N(CH_3)_3Cl + OH^-$



Source: Pearson Study 2008

7. Chemical and Microbiological Contamination

Dissolved Ions - Coloured Cations

Iron in the groundwater

Fe^{2+} under anaerobic conditions:	light green
Fe^{3+} under aerobic conditions:	yellow-red-brown

$4\ Fe^{2+}(aq) + O_2(aq) + 10\ H_2O(l) \rightarrow 4\ Fe(OH)_3(s)\downarrow + 8\ H^+(aq)$

Removal: Filtration or flocculation

Felling with $PO_4^{3-}(aq) \rightarrow FePO_4(s)\downarrow$

Manganese in the groundwater

Mn^{2+} under anaerobic conditions:	light pink
Mn^{4+} under aerobic conditions:	brown

$2\ Mn^{2+}(aq) + O_2(aq) + 2\ H_2O(l) \rightarrow 2\ MnO_2(s)\downarrow + 4\ H^+(aq)$

Removal: Filtration or flocculation

Reduction with $Mn(s) + MnO_2(s) + 4\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 2\ H_2O(l)$

Source: DVGW Worksheet W 223, 2005: Iron and manganese removal

7. Chemical and Microbiological Contamination

Dissolved Ions - Uranyl Cations $[O=U=O]^{2+}$

- Mineral phosphate fertilizers contain on average between 50 and 100 mg uranium per kg fertilizer [1], corresponding to 50 - 100 ppm
- The drinking water limit value is 10 µg/l [2], which corresponds to an intake of over 7 mg uranium per year (Ore Mountains, assumed water intake: 2 liter/day)
- Between 1951 and 2011, 14,000 metric tons of uranium were spread on German fields, i.e. 233 tons/year [3]

Removal: 1. Reduction to U^{4+}
2. Precipitation with phosphate as $[U(HPO_4)_2]\downarrow$

Literature

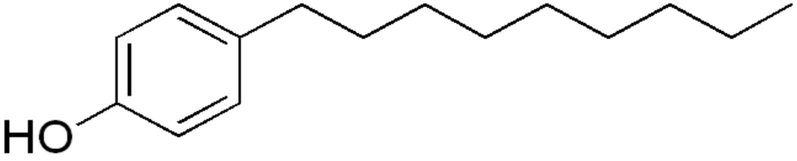
[1] Umweltbundesamt, Text 37/2012
[2] Uranium in German Tap and Groundwater, in: The New Uranium Mining Boom, Springer 2011, S. 807-820
[3] Strahlentelex, Nr. 612-613 (2012) 3

7. Chemical and Microbiological Contamination

Pharmaceuticals, Diagnostics and Personal Care Products

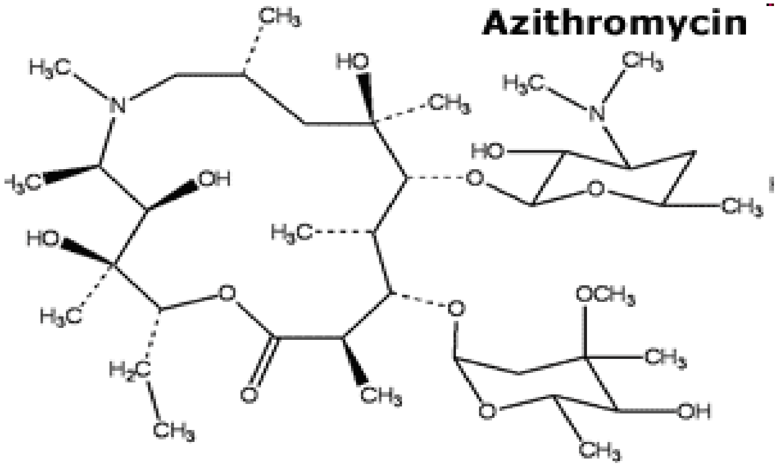
- **Human activity: cosmetics, shaving creams, soaps, UV protection products, …**
- **Illegal drugs**
- **Veterinary drugs, especially antibiotics and steroids**
- **Residues from pharmaceutical production → Industrial wastewater**
- **Wastewater from hospitals, clinics, doctors' surgeries, etc. → Gd^{3+} exposure through NMR displacement reagents (Gd^{3+}- complexes), contrast agents (iodides)**

Detergens



4-n-Nonylphenole

Antibiotics

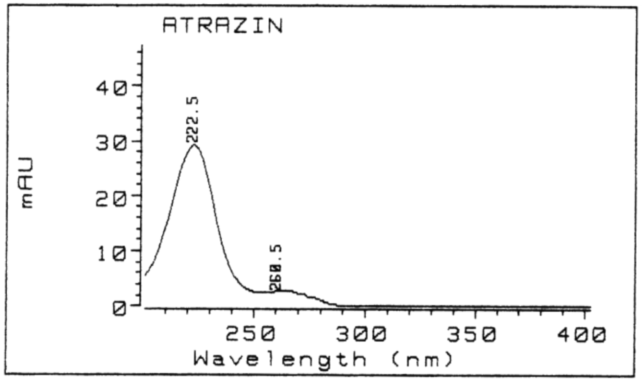


7. Chemical and Microbiological Contamination

Pesticide Residues - Dependent on Utilisation and Degradation Mechanisms

Classification

• Avicides	against birds
• Bactericides	against bacteria
• Fungicides	against fungi
• Herbicides	against weeds
• Insecticides	against insects
• Molluscicides	against snails
• Nematicides	against threadworms
• Rodentizide	against rodents
• Virucidal	against viruses



Non-halogenated substances are completely degraded

Chlorinated insecticides, on the other hand, degrade only slowly, such as Aldrin, Atrazine, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Mirex and so on

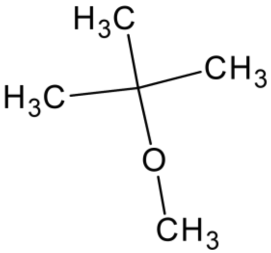
Organophosphorus compounds are now frequently used…..

7. Chemical and Microbiological Contamination

Oil Products and their Residues

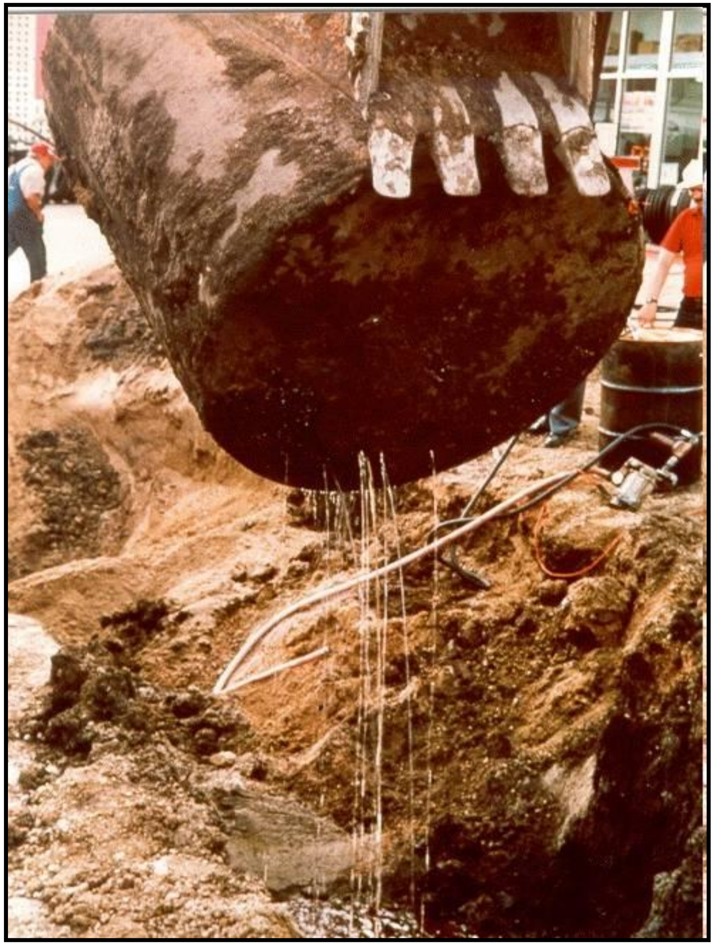
- BTEX – Benzene, toluene, ethylbenzene and xylene

- MTBE – Methyl-tert.-butyl ether
  Very soluble in water



- Used engine oils

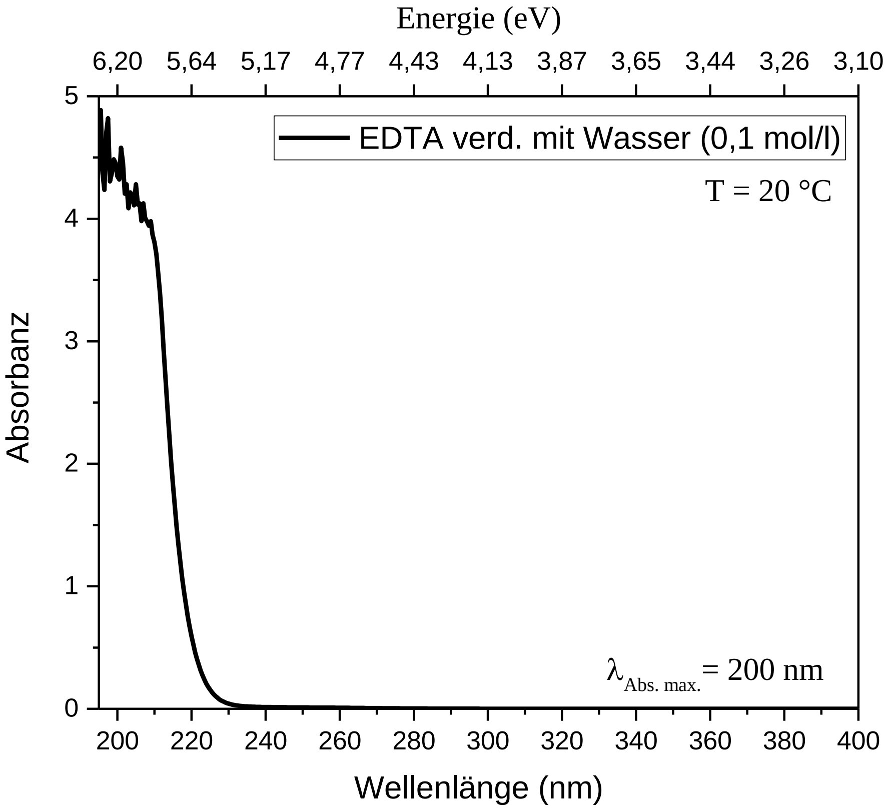
- “Total Petroleum hydrocarbons” TPH
  - Petrol
  - Diesel
  - Crude oil



7. Chemical and Microbiological Contamination

Other Micropollutants

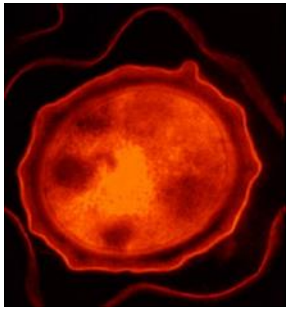
- Perfluorinated tensides
- Flame retardants
- Complexing agents, e.g. EDTA
- Illegal drugs
- Odourants
- Fracking residues
- Contaminated sites, e.g. explosives



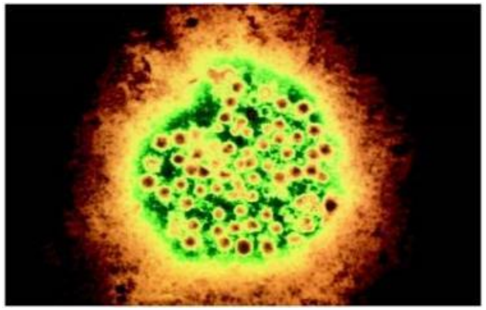
→ **Up to 8,000 different micropollutants are now recorded**

7. Chemical and Microbiological Contamination

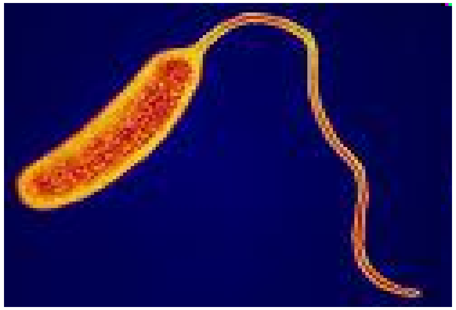
Microbiological Contamination is a Threat to Public Health



Anthrax spore



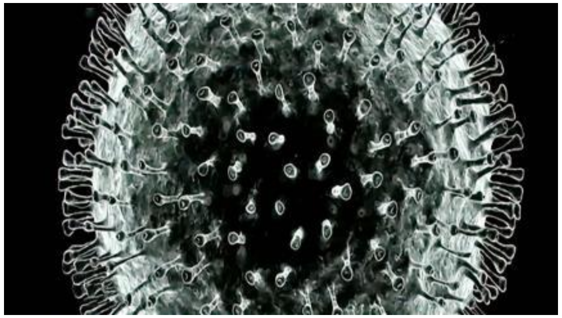
Hepatitis A



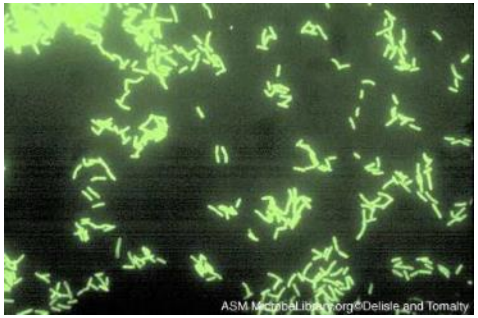
Cholera

Amoebae

Cryptosporidium



Coronavirus



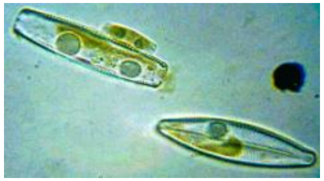
ASM MicrobeLibrary.org©Delisle and Tomalty

Legionella pneuomophila

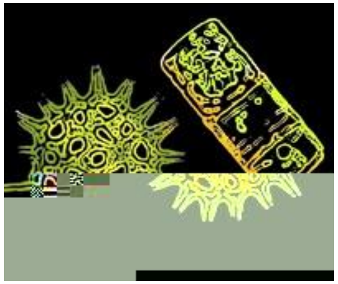
Giardia

7. Chemical and Microbiological Contamination

Odour and Taste of Surface Water - Lakes, Rivers, Streams, etc.



- **Algae: Diatoms, blue-green algae, flagellates**



- **Actinomycetes: Filamentous bacteria**
    - **Earthy flavor**
    - **Compounds: Geosmin and 2-methylisoborneol**
    - **Removal: coagulation, filtration, oxidation**

- **Disinfection by-products: Chlorine compounds**
    - **By chlorination of natural organic matter (NOM: fulvic and humic acids)**
    - **Compounds: Trihalomethane: Trihalomethan (THM: $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$)**
    - **Removal: Oxidation of NOM by ozone, UV irradiation, adsorption with activated carbon**

7. Chemical and Microbiological Contamination

Smell and Taste of Surface Water - Sea

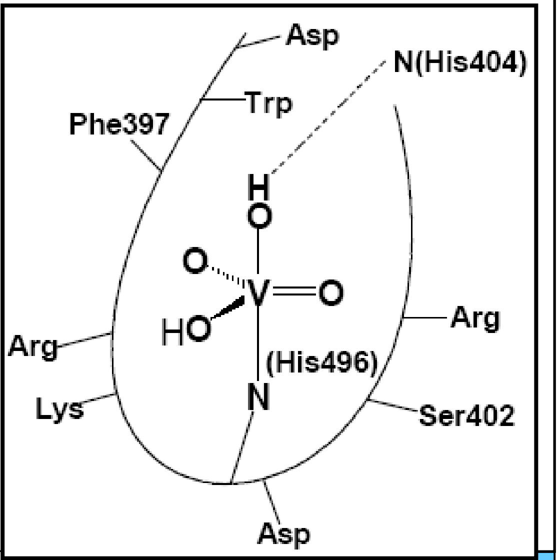
Aerosols: NaCl, $MgCl_2$, Bromides, ….

<u>Organobromine compounds and sulphoxides</u>

Formation by haloperoxidases,

e.g. in knotted kelp (Ascophyllum nodosum):

These contain vanadium(V) ions in their active form

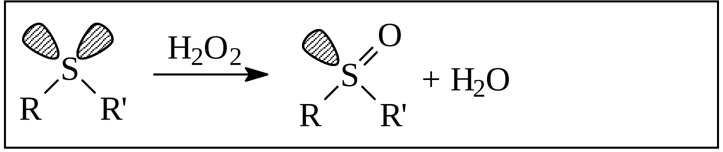


$$H_2O_2 + Br^- + H^+ \rightarrow HOBr + H_2O$$

$$HOBr + R\text{-}H \rightarrow 2\ R\text{-}Br + H_2O$$

$$HOBr + H_2O_2 \rightarrow {}^1O_2 + H_2O + Br^- + H^+$$

$$Br^- + HOBr + H^+ \rightarrow H_2O + Br_2$$



→ Orientation of seabirds to find the coastal line

7. Chemical and Microbiological Contamination

Measured Variables for Assessing Water Quality - Ions and Dissolved Substances

• **Alkalinity**	**Acid neutralization capacity**
• **Acidity**	**Base neutralization capacity**
• **Hardness**	Ca^{2+}**- and** Mg^{2+}**-Salts**
• **pH-value**	**Acidity**
• **Dissolved org. compounds**	**Humic acids**
• **Salinity**	Na^+ , Cl^-
• **Cations**	Na^+, K^+, Ca^{2+}, Mg^{2+}
• **Anions**	Cl^-, HCO_3^-, SO_4^{2-}, NO_3^-
• **Heavy metals**	**Cr, Fe, Co, Ni, Cu, Zn, Cd, Hg, Sn, Pb, As, Sb, U, …**

8. Cleaning Methods - An Overview

Chemical and Physical Methods

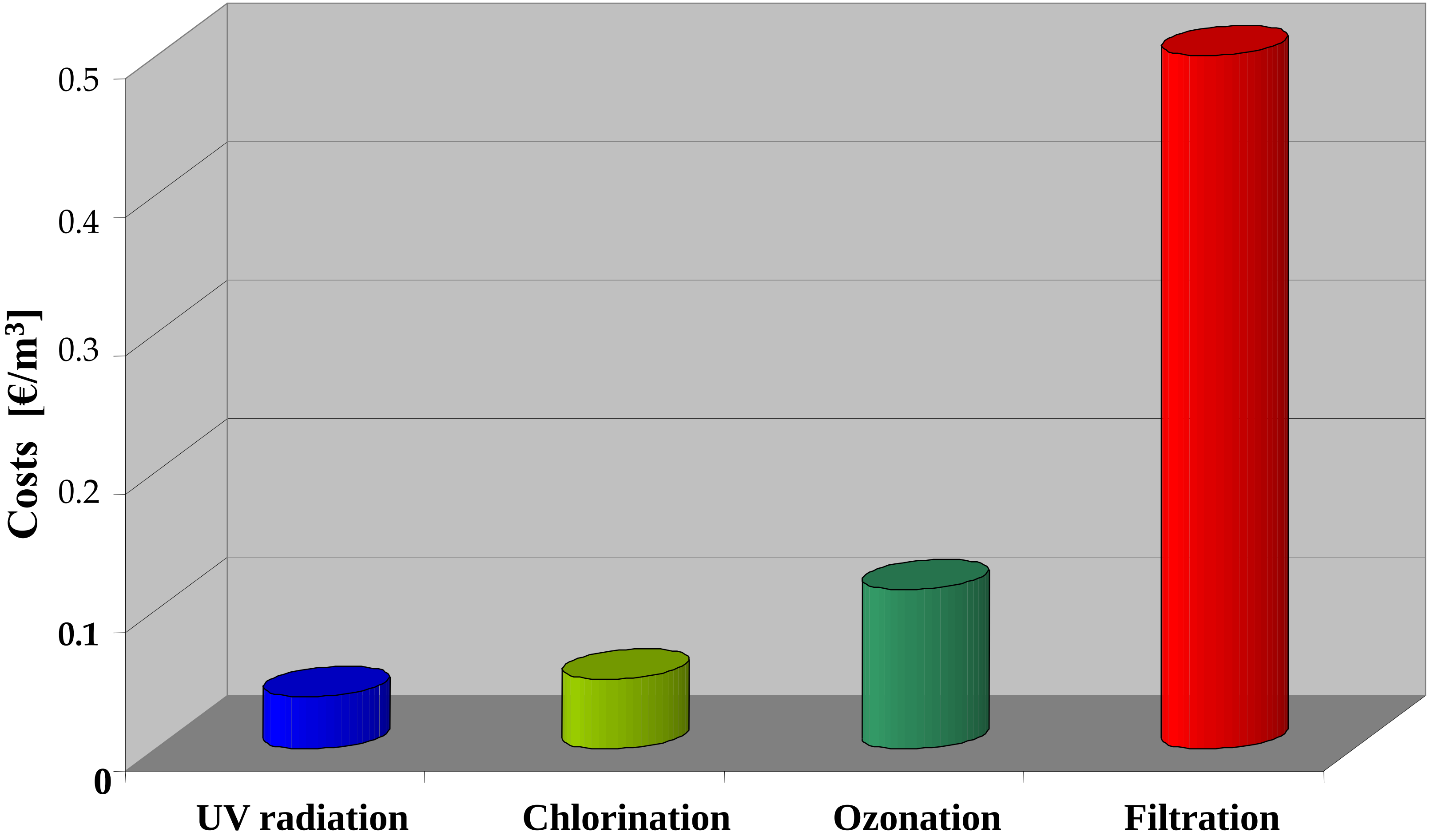
Waste, surface and process water treatment

- **Physical methods**
  - Heating
  - Distillation
  - Sedimentation
  - Filtration
  - Membrane filtration
  - Adsorption (active carbon)
  - "Biological"
  - Photovoltaic
  - Flocculation
  - Coagulation
- **Chemical methods**
  - **Non-green chemistry**
    - Chlorination (Cl_2)
    - Chlorine dioxide addition (ClO_2)
  - **Green chemistry**
    - Catalytic oxidation with Fe-TAML/H_2O_2
    - Advanced oxidation processes
      - Fenton-Oxidation
      - Heterogeneous photocatalysis
      - Electrolysis
      - Sonolysis
      - Oxygen singlet
      - O_3
      - H_2O_2
      - UV

TAML = Tetraamidomacrocyclic ligand

8. Cleaning Methods - An Overview

Chemical and Physical Methods



Source: “Disinfection of biologically treated wastewater”, Merkpaper ATV-M 205, German Association for Water, Wastewater and Waste e.V. (1998)

8. Cleaning Methods - An Overview

(Vacuum) UV-Irradiation - Advantages

- Direct method: effective, economical, selective
- Simple Installation
- Side effect: Inactivation of microorganisms such as Cryptosporidium Parvum oocysts, Giardia Muris and so on
- Safe and easy handling
- No use of hazardous chemicals
- Minimal formation of by-products
- No influence on the odor and/or taste of water or air
- No concentration or accumulation of viruses, bacteria, spores, fungi, …

8. Cleaning Methods - An Overview

Disinfection Methods - Application and Terms

Disinfection always takes place at the end of the water treatment chain

- **Coagulation**
- **Flocculation**
- **Sedimentation**
- **Filtration**
- **Disinfection**

Some terms

Sterilisation	**Complete elimination of microorganisms**
Desinfection	**Reduction of the bacterial count, e.g. by factor of 10000 (→ log4 reduction)**
Bactericide	**Substance that reduces the bacterial count, e.g. chlorine**
Bacteriostatic	**Substance that stops the multiplication of germs, e.g. copper**
Planktonic	**Individually present microorganisms**
Intracellular	**Microorganisms in a cell, e.g. in an amoeba**

8. Cleaning Methods - an Overview

Methods of Disinfection

- Thermal treatment (boiling, distillation)
  - At home and in emergency situations (outdoor activities)
- Chlorination → $Cl_2(g)$, $NaOCl(l)$ or $Ca(OCl)_2(s)$
- Addition of monochloramine → NH_2Cl
- Ozonisation → O_3
- Adding chlorine dioxide → ClO_2
- UV-radiation
  - Solar radiation
  - Hg emitter
  - Excimer emitter
  - LED, laser diodes
- Iodine addition
  - Only for a short time
  - Harmful to health in the long term

9. Physical Methods of Water Treatment

Filtration Methods

Goal: Elimination of suspended substances: $d_{50} > 100$ nm, colloids $d_{50} < 100$ nm

Significance: Central element of every drinking water treatment plant (usually three stages)

Filtration types:

Rapid filtration

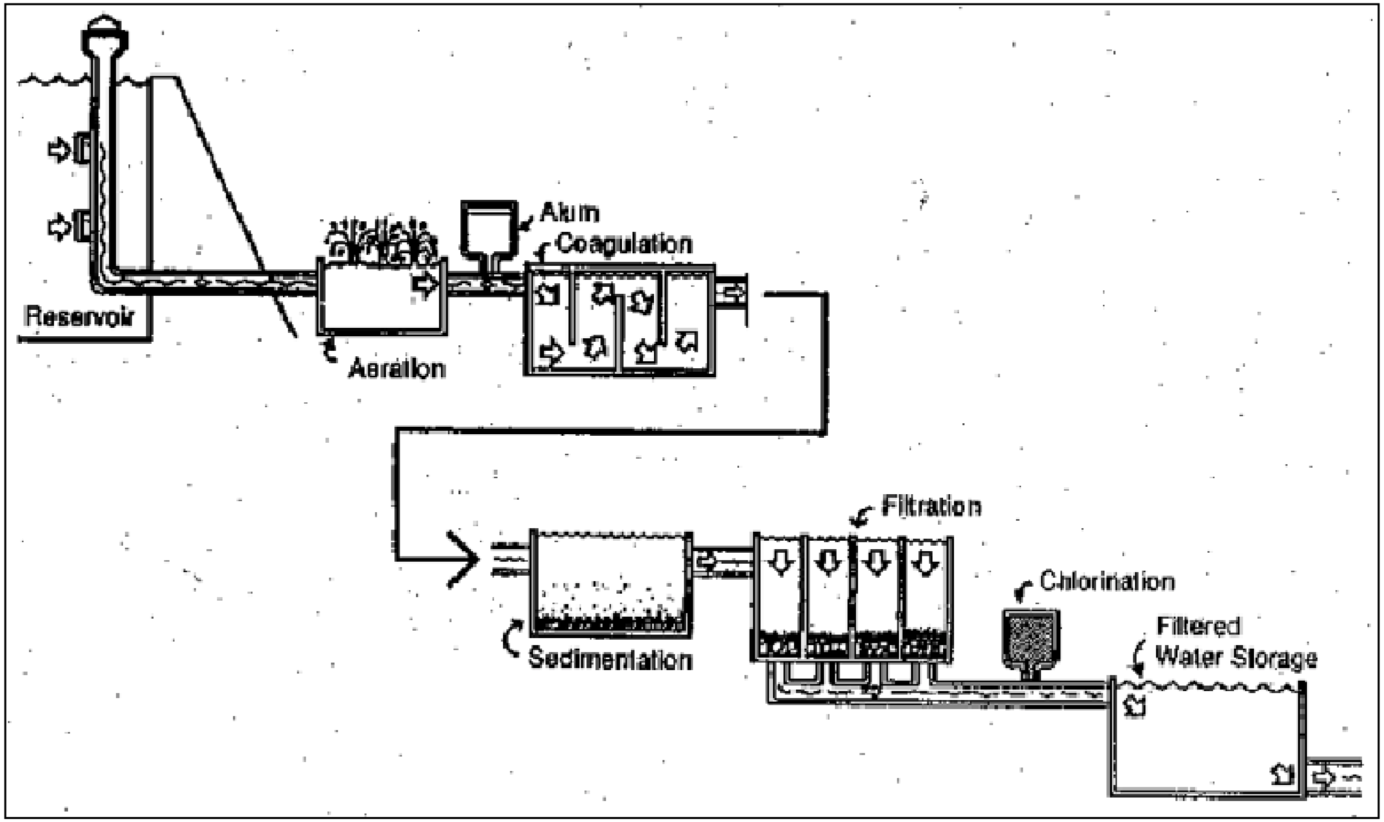
Slow sand filtration

Gravity filtration

Pressure filtration

Single-layer filtration

Multilayer filtration



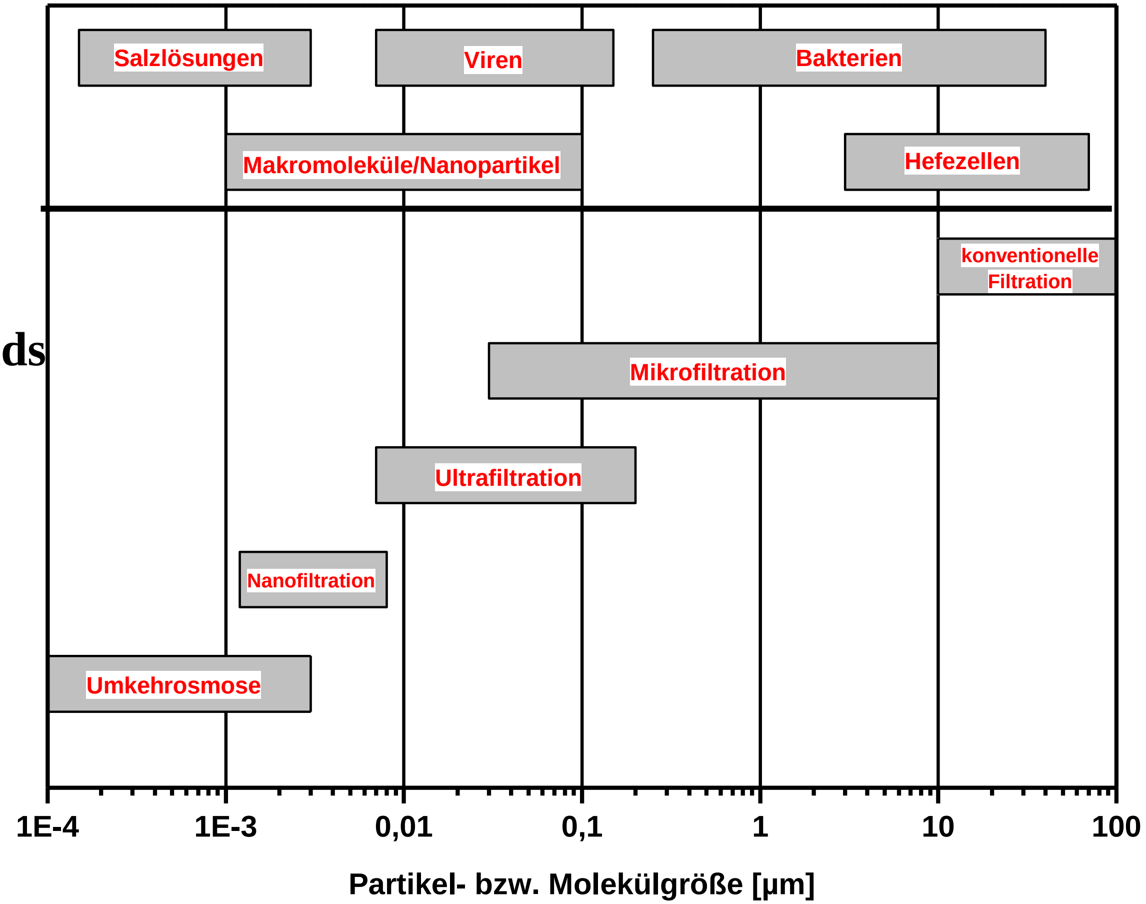
9. Physical Methods of Water Treatment

Filtration Methods

Variables that determine the filtration process and its speed:

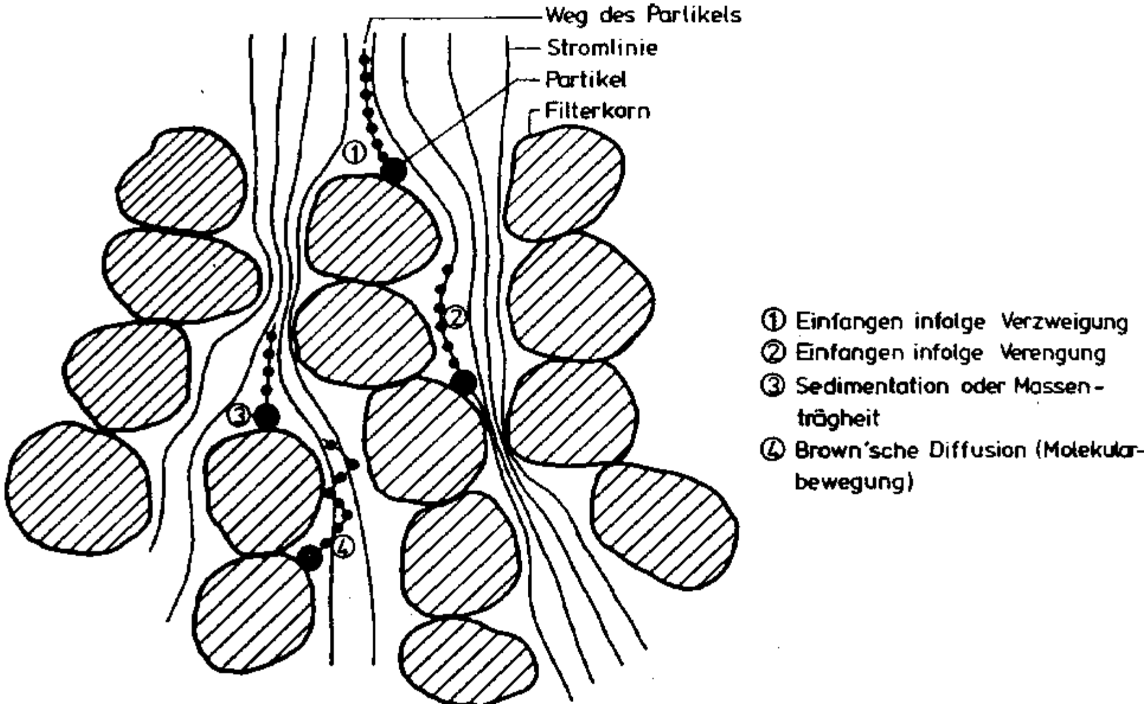
- Particle size
- Pressure
- Grain size of the filter material or materials
- Height of the filter layer or layers
- Chemical pre-treatment of the solids to be filtered

Particle size and filtration method



9. Physical Methods of Water Treatment

Filtration Methods



Physical filtration principle
- **Flow resistance**
- **Adsorption and desorption**

Filter structure:
- **Grain type: sand, activated carbon**
- **Grain size**
- **Filter bed height**
- **Overflow height**

Parameters for assessing performance
- **Overflow height**
- **Filter size: surface area, volume**
- **Filter speed**
- **Running time of the filter: Time until breakthrough**
- **Water properties: viscosity, density**

Phosphate Reduction PO_4^{3-}

Method: Addition of precipitants or flocculants (Fe^{3+}, Al^{3+}, Ca^{2+})

Fe^{3+} as $FeCl_3$ or $Fe_2(SO_4)_3$
Al^{3+} as $Al_2(SO_4)_3$
Ca^{2+} as $CaCl_2$

$Fe^{3+} + PO_4^{3-} \rightleftharpoons FePO_4\downarrow$ $pK_L = 26$

$Al^{3+} + PO_4^{3-} \rightleftharpoons AlPO_4\downarrow$ $pK_L = 21$

$3\ Ca^{2+} + 2\ PO_4^{3-} \rightleftharpoons Ca_3(PO_4)_2\downarrow$ $pK_L = 32$

$5\ Ca^{2+} + 3\ PO_4^{3-} + F^- \rightleftharpoons Ca_5(PO_4)_3F\downarrow$ $pK_L = 45$

$Mg^{2+} + NH_4^+ + PO_4^{3-} \rightleftharpoons MgNH_4(PO_4)\cdot 6H_2O\downarrow$ **“Struvite”**

After separation, the precipitation products are channeled for further use!

10. Chemical Methods of Water Treatment

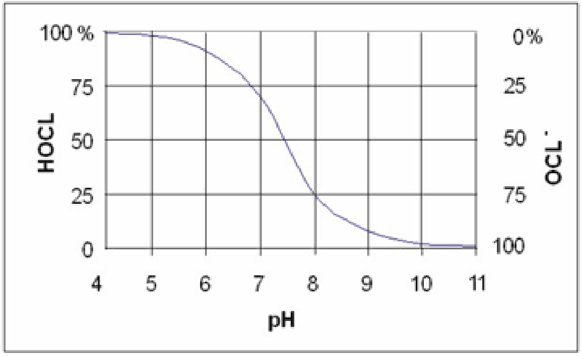
Chlorination Cl_2

Historical: First application London, GB in 1905

Maximum recommended Cl_2- concentration: < 5 mg/l (USA, EPA)
< 1.2 mg/l (D, DIN EN937)

Source materials for chlorination:

- **Cl_2 (gas)**
- **NaOCl (Liquid)**
- **$Ca(OCl)_2$ (Solids)**
- **NaCl (solved): Electrochlorination $2\ Cl^- \rightleftharpoons Cl_2 + 2\ e^-$**

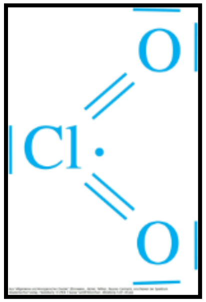


In alkaline solution: $Cl_2 + 2\ OH^- \rightleftharpoons OCl^- + Cl^- + H_2O$ Disproportionation

- **OCl^- (Hypochlorite) is a strong oxidizing agent**
- **$OCl^- + NH_3 \rightleftharpoons HO^- + NH_2Cl$ (Chloramine → Swimming pool odour!)**

10. Chemical Methods of Water Treatment

Addition of Chlorine Dioxide $Cl^{+IV}O_2$



History: First application in Niagara Fall, NY, USA in 1944

Maximum recommended ClO_2- concentration: **< 0.5 mg/l (USA, EPA)**
< 0.4 mg/l (D)

Representation (mostly centralised from solid chemicals)

- $2\ NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2\ ClO_2 + 2\ NaHSO_4$
- $2\ NaClO_2 + Cl_2 \rightarrow 2\ ClO_2 + 2\ NaCl$

Properties

- **In alkaline solution** $2\ ClO_2 + 2\ OH^- \rightleftharpoons ClO_2^- + ClO_3^- + H_2O$ **Disproportionation**
- **Thermal decomposition** $2\ ClO_2 \rightarrow Cl_2 + 2\ O_2$

10. Chemical Methods of Water Treatment

Addition of Chloramine NH_2Cl

History: First application in Ottawa, Canada and Denver, CO, USA in 1917

Recommended NH_2Cl- concentration: Some mg/l (USA, EPA)

Representation (mostly from hypochlorite and ammonium chloride)
- $HOCl + NH_3 \rightleftharpoons NH_2Cl + H_2O$

Properties
- **Only stable between pH 7 and 9**
- **Moderate oxidation potential**

10. Chemical Methods of Water Treatment

Ozonation O_3

History: First application in Oudshoon, USA in 1893

Representation

1. **Siemen's ozoniser (1857)**
2. **Hg discharge lamps**
3. **Silent discharges in dry air (ozone generators)**

Applications

- **Advanced Oxidation Processes (AOP): Combination of UV-C with O_3**
- **Odor removal (old clothing)**
- **Sterilisation**
- **Ozonolysis**

Maximum recommended O_3 concentration: < 10 mg/l

11. Photochem. Methods of Water Treatment

Classification of UV-Radiation

VUV	UV-C	UV-B	UV-A

100 nm 200 nm 280 nm 315/320 nm 400 nm

12.5 – 6.9 eV	6.2 – 4.5 eV	4.5 – 3.9 eV	3.9 – 3.1 eV
Splitting of H_2O and O_2 into radicals Ozone formation Cleavage of C-C, C-H, C-O bonds	Excitation of C=C bonds Excitation of the nucleobases Cleavage of O_3, ClO_2 and H_2O_2	Vitamin D formationTranscription of repair enzymes Formation of melanosomes in the skin	Photocatalytic reactions Oxidation of melanin in the skin Decomposition of organic pigments Activation of photocatalytic pigments
Waver cleaning Photochemistry	Disinfection of air, H_2O and surfaces Photochemistry	Treatment of skin diseases (psoriasis) Tanning Photochemistry	Water and air purification using TiO_2 photocatalyst Tanning Photochemistry

11. Photochem. Methods of Water Treatment

Chemical Bonding and Photon Energy

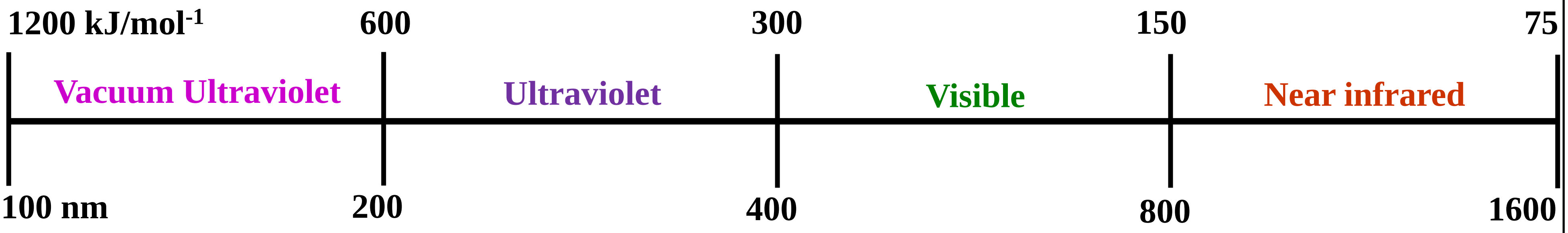
Energy of chemical bonds

~ 10 – 1100 kJ/mol

E-E	100 – 500 kJ/mol	F-F C-C	159 kJ/mol 348 kJ/mol
E=E	400 – 700 kJ/mol	O=O C=C	498 kJ/mol 648 kJ/mol
E≡E	800 – 1100 kJ/mol	N≡N C≡C	946 kJ/mol 839 kJ/mol
H-bridges	10 - 160 kJ/mol	H...F > H...O > H...N	
Van-der-Waals	0.5 - 5 kJ/mol		

Energy of optical radiation

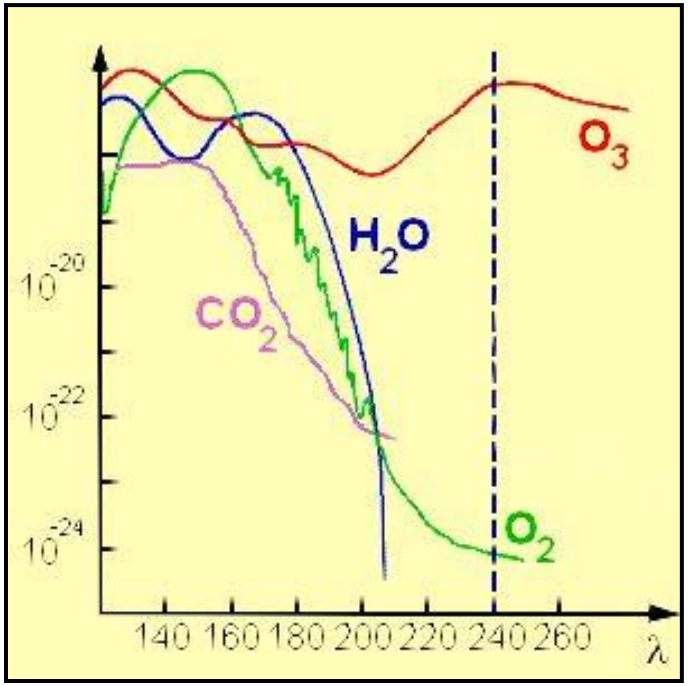
$$E = N_A hc/\lambda = 119226/\lambda \quad [\mathrm{kJmol^{-1}}]$$



(V)UV - VIS radiation can therefore split chemical bonds

11. Photochem. Methods of Water Treatment

UV-Radiation - Effect on Water and Air Components



1. photochemical splitting of water

$H_2O + h\nu(< 200\ \text{nm}) \rightarrow OH^{\cdot} + H^{\cdot}$

$2\ OH^{\cdot} \rightarrow H_2O_2$

$2\ H_2O_2 \rightarrow 2\ H_2O + {}^1O_2 \rightarrow {}^3O_2 + \text{Energy!}$

2. Ozone formation

${}^3O_2 + h\nu(< 200\ \text{nm}) \rightarrow 2\ O^{\cdot}$

$2\ O_2 + 2\ O^{\cdot} \rightarrow 2\ O_3$ (no radical)

3. Photochemical splitting of ozone

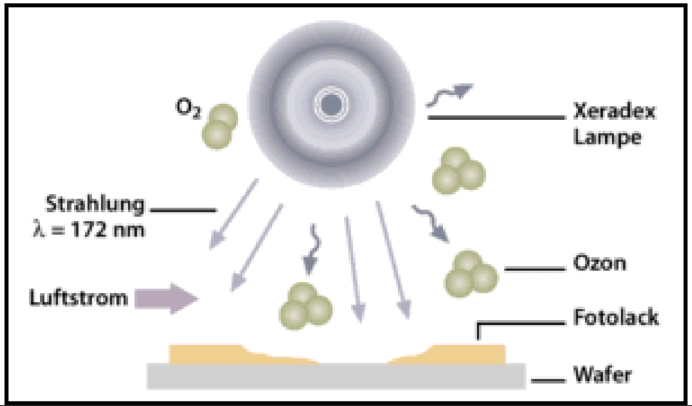
$O_3 + h\nu(< 320\ \text{nm}) \rightarrow {}^1O_2 + {}^1O$

4. Photochemical decomposition of carbon dioxide

$CO_2 + h\nu(< 200\ \text{nm}) \rightarrow CO + O^{\cdot}$

5. Photochemical splitting of nitrogen

$N_2 + h\nu(< 120\ \text{nm}) \rightarrow 2\ N^{\cdot}$

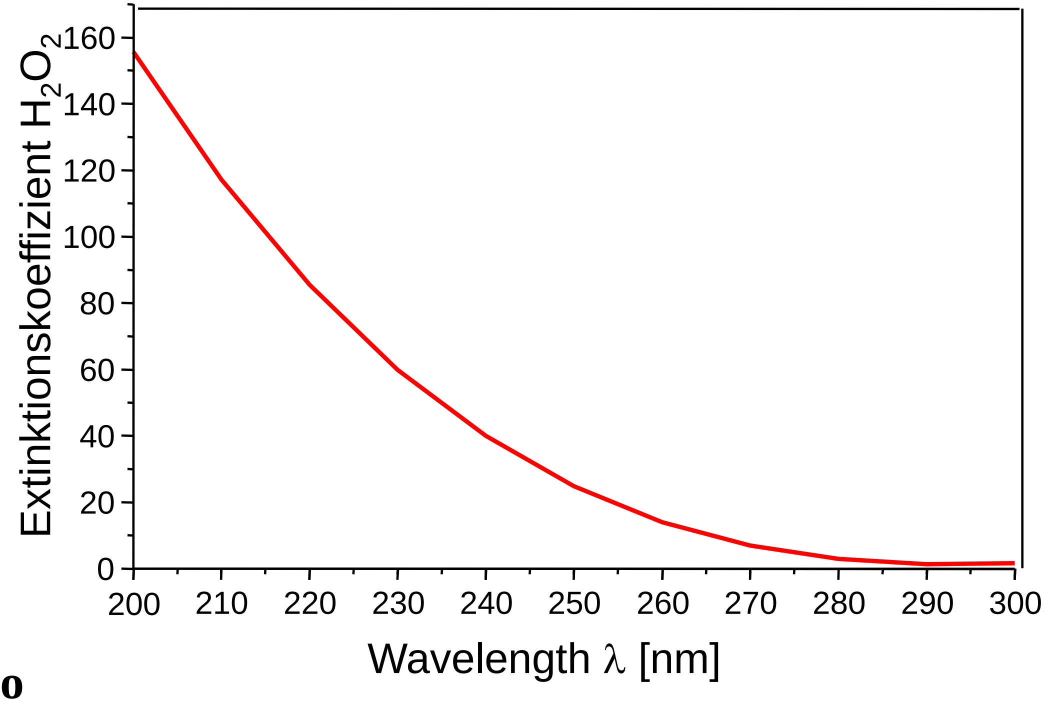


11. Photochem. Methods of Water Treatment

UV-Radiation - Effect on H_2O_2 and O_3

1. Splitting of H_2O_2 into OH radicals (H_2O_2/UV process)

$H_2O_2 + h\nu(< 280\ nm) \rightarrow 2\ OH^{\cdot}$



2. Conversion of ozone into H_2O_2

$O_3 + H_2O + h\nu(< 330\ nm)$

$\rightarrow H_2O_2 + O_2$

$H_2O_2 + h\nu(< 280\ nm) \rightarrow 2\ OH^{\cdot}$

The formation of $OH^{\cdot}$ radicals is the key to

"Advanced Oxidation Processes" (AOPs): $OH^{\cdot} + M \rightarrow OH^- + M^+$

11. Photochem. Methods of Water Treatment

UV-Radiation - Effect on other Inorganic Molecules

- **Splitting of HCOOH**

  $HCOOH + h\nu(< 260\ nm) \rightarrow CO + H_2O$

- **Dismantling of CN^-**

  $2\ CN^- + O_2 + h\nu(< 280\ nm) \rightarrow 2\ OCN^-$

- **Splitting of NO_3^-**

  $2\ NO_3^- + h\nu(< 240\ nm) \rightarrow 2\ NO_2^- + O_2$
  $NO_3^- + H^+ + h\nu(172\ nm) \rightarrow NO_2 + OH\cdot$

- **Splitting of NO_2^-**
  $NO_2^- + H^+ + h\nu\ (< 365\ nm) \rightarrow NO + OH\cdot$

- **Splitting of Azides**

  $2\ NaN_3 + h\nu(< 300\ nm) \rightarrow 2\ Na + 3\ N_2$ Ergo: $2\ Na + 2\ H_2O \rightarrow 2\ Na^+ + H_2 + 2\ OH^-$

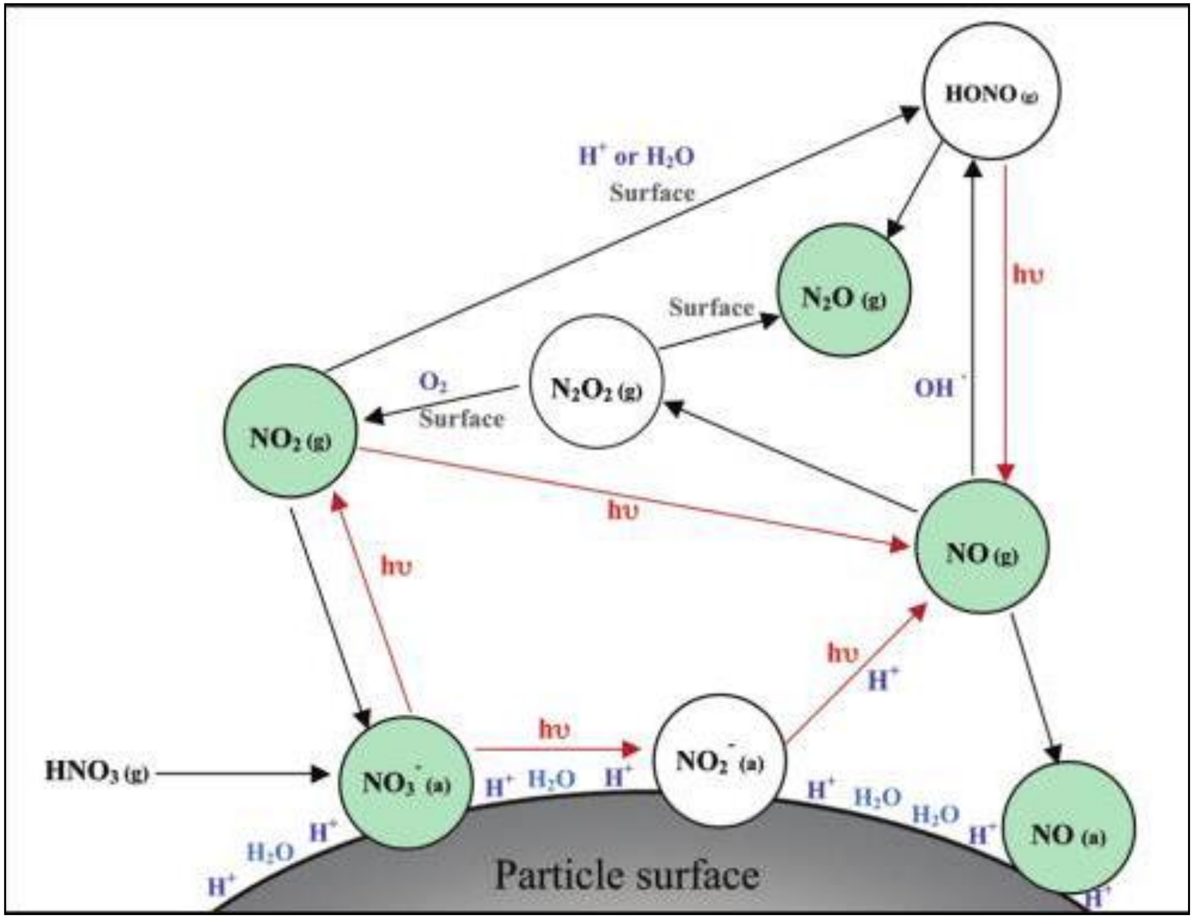
11. Photochem. Methods of Water Treatment

UV-Radiation - Effect on Inorganic Molecules

Complex chemical equilibrium equilibrium between various NO_x- and NO_x^- - species

For instance: $NO_2^- + 2 H^+ + e^- \rightarrow NO(g) + H_2O$ at 365 nm

By product: N_2O (climate active trace gas)



11. Photochem. Methods of Water Treatment

UV-Radiation - Effect on Organic Molecules

- **Splitting of organoazide compounds**

  $R\text{-}N{=}N{=}N + h\nu(< 300\ \text{nm}) \rightarrow R{=}N + N_2$

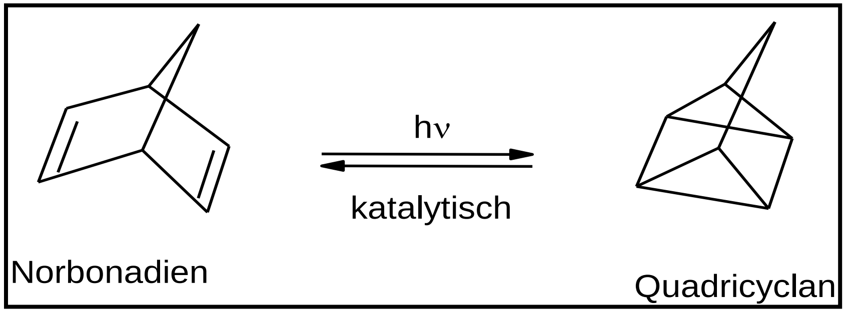
- **Splitting of diazo compounds**

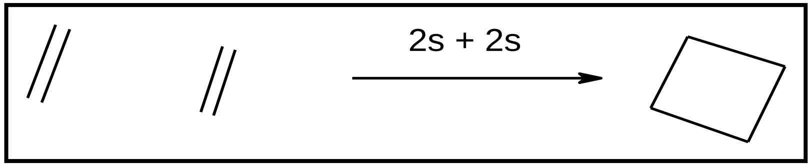
  $R\text{-}CO\text{-}CH{=}N{=}N + h\nu(< 350\ \text{nm}) \rightarrow R\text{-}CH{=}C{=}O + N_2$

- **Splitting of peroxides**

  $R\text{-}O\text{-}O\text{-}R + h\nu(< 400\ \text{nm}) \rightarrow 2\ R^{\cdot} + O_2 \rightarrow$ Radical chain reactions: „Photocuring“

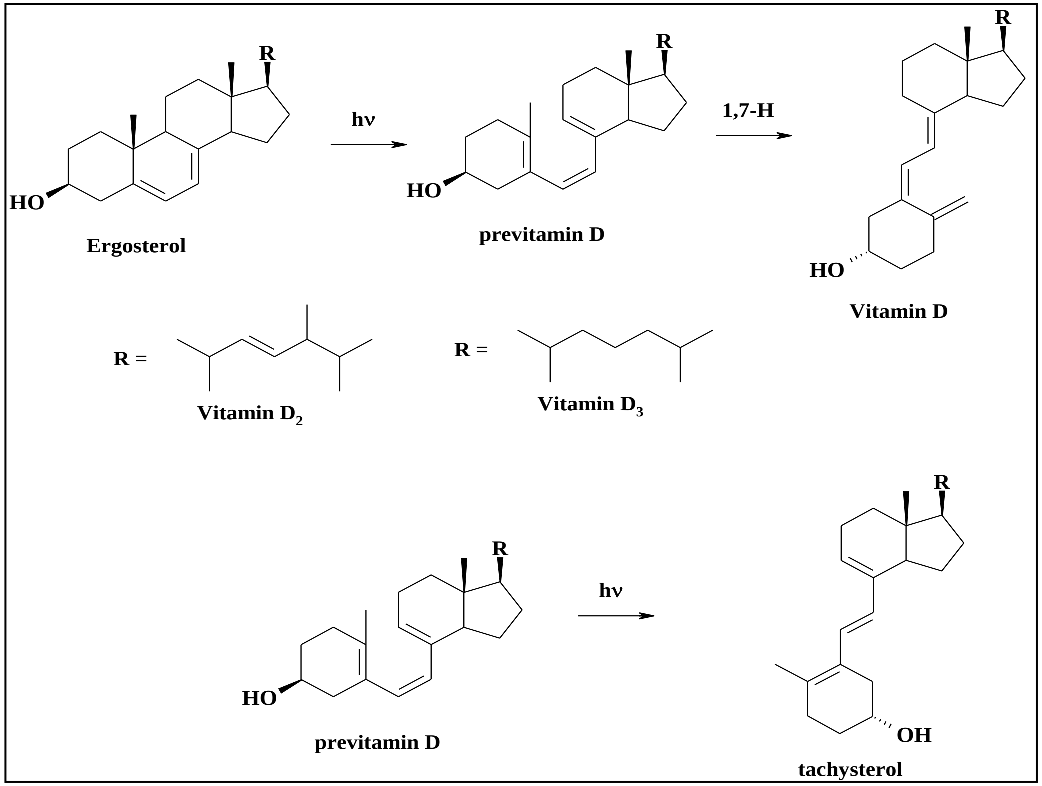
- **[2+2] Cycloaddition according to Woodward-Hoffman rules for electrocyclic reactions.**





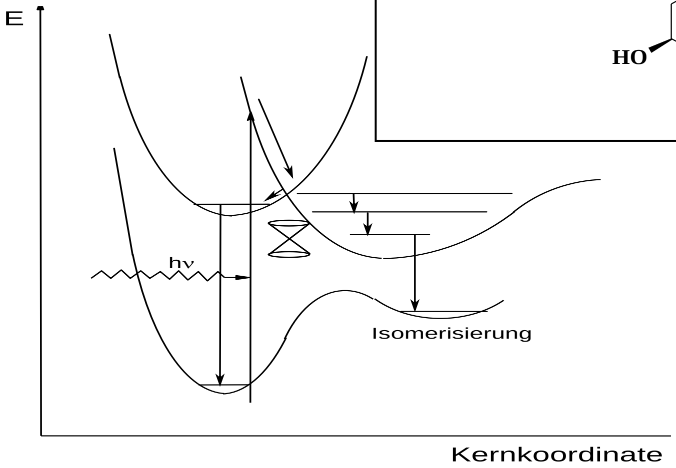
11. Photochem. Methods of Water Treatment

UV-Radiation - Effect on Organic Molecules



- **Photoisomerisation:**
  Praecalciferol + hν (282 nm)
  → Calciferol (Vitamin D_3)

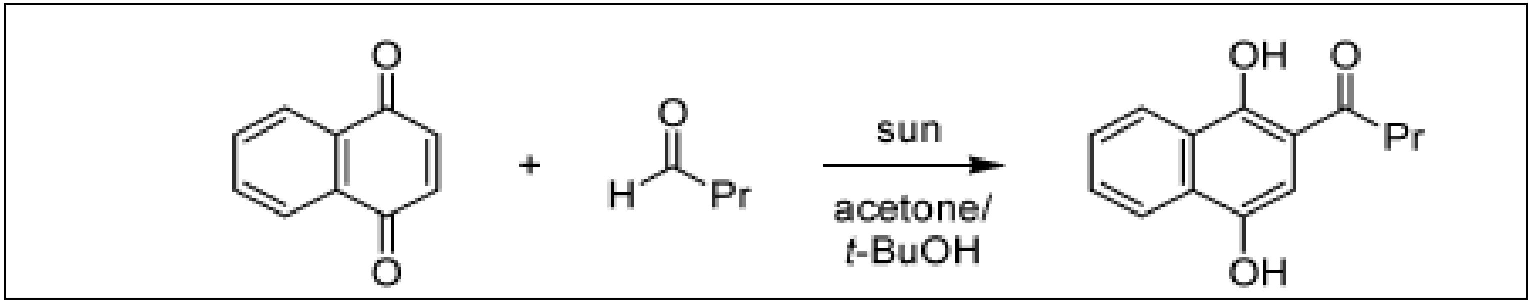
- **Photodegradation (Bleach):**
  Reaction with $^1O_2$ (Singlet-oxygen)
  → Addition to double bonds



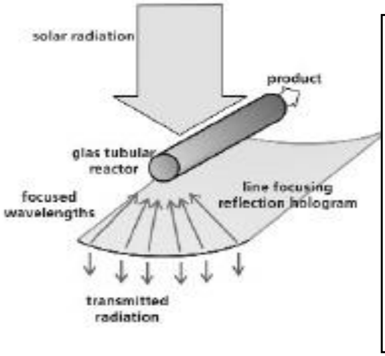
11. Photochem. Methods of Water Treatment

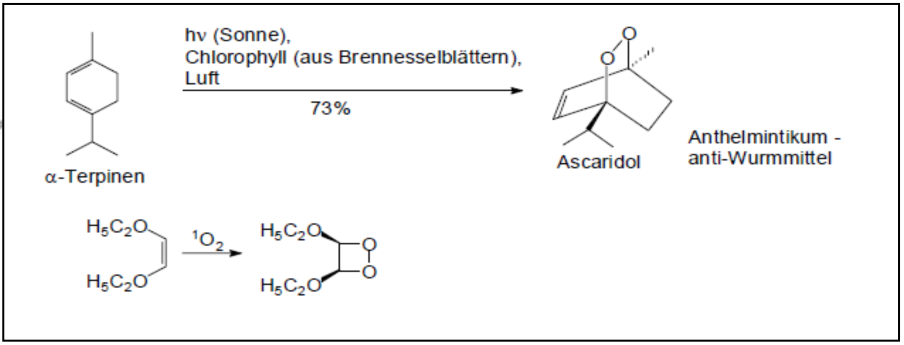
UV-Radiation - Effect on Organic Molecules

- Photoinduced acylation of aromatic compounds



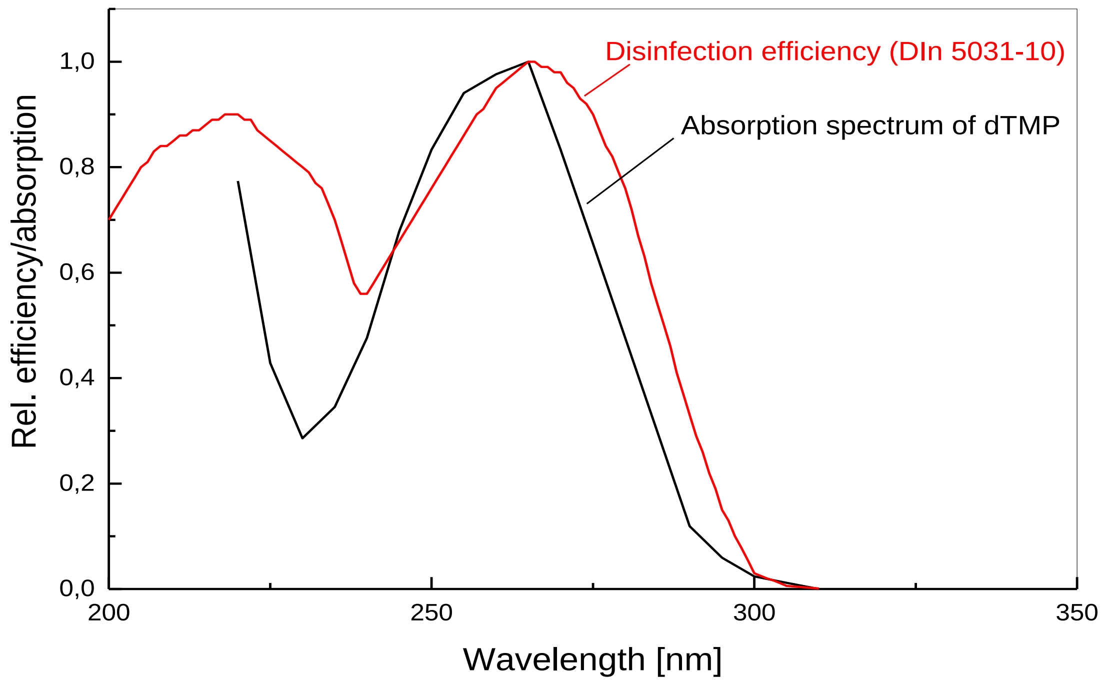
- „ Solar chemistry in flow-through reactors“

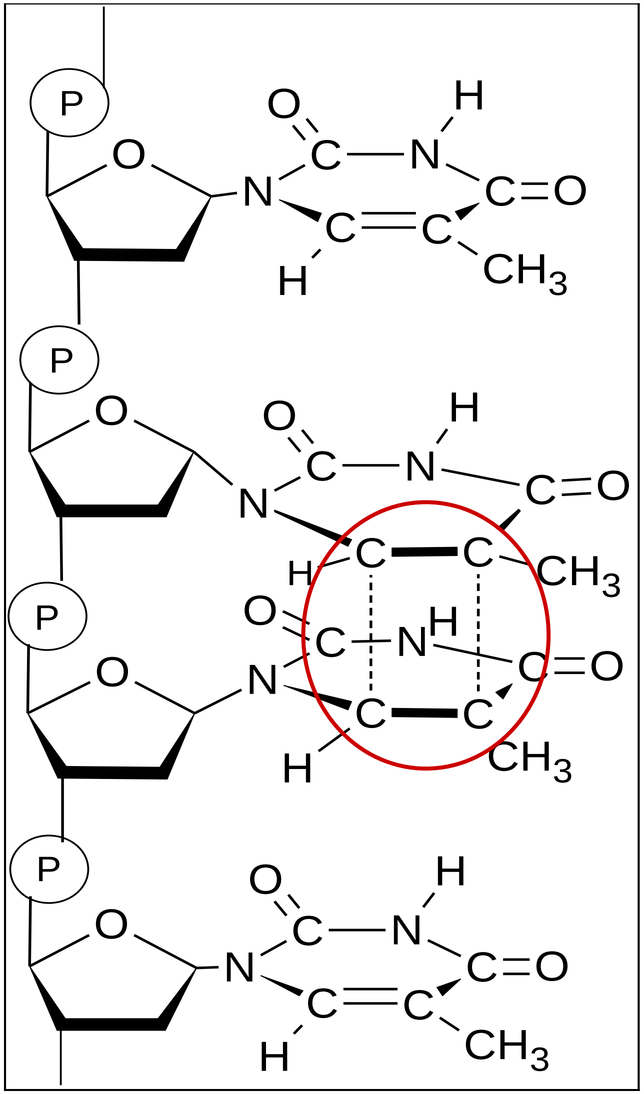




11. Photochem. Methods of Water Treatment

UV-Radiation - Effect on Biochemical Molecules



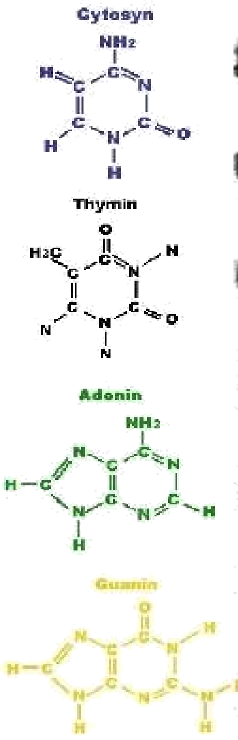


Nucleotide	Extinction coefficient ε by 260 nm
dAMP	15,200 $lmol^{-1}cm^{-1}$
dTMP	8,400 $lmol^{-1}cm^{-1}$
dGMP	12,000 $lmol^{-1}cm^{-1}$
dCMP	7,100 $lmol^{-1}cm^{-1}$

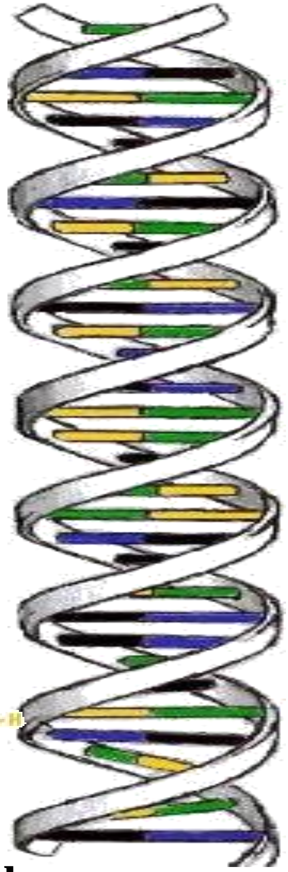
11. Photochem. Methods of Water Treatment

UV-Radiation - Effect on Biochemical Molecules

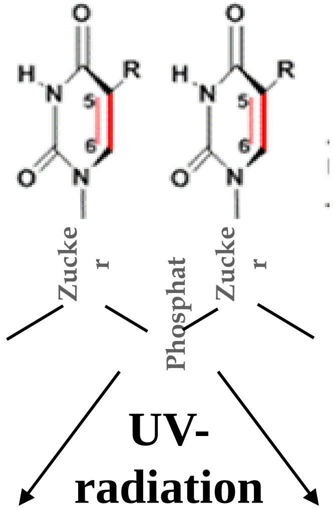
Bases

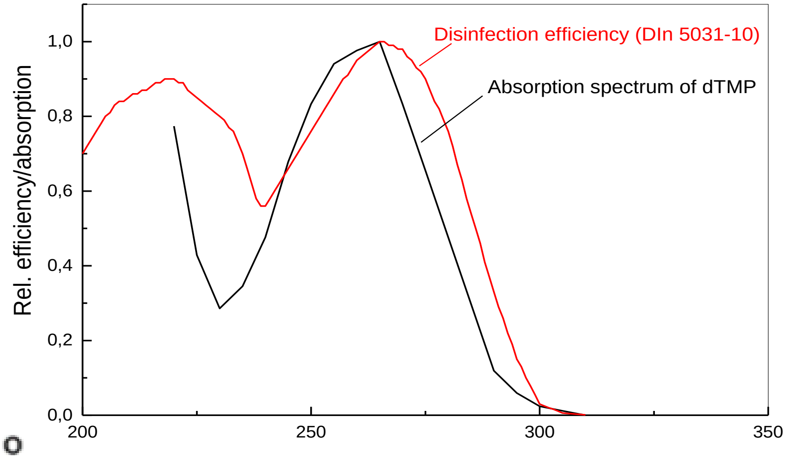


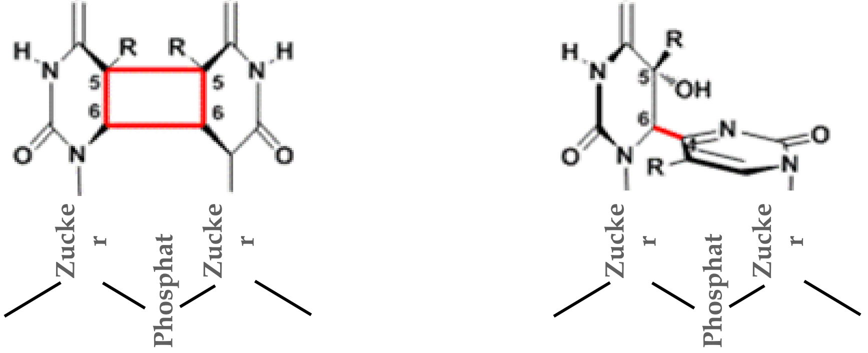
Double helix



Neighbouring thymine bases





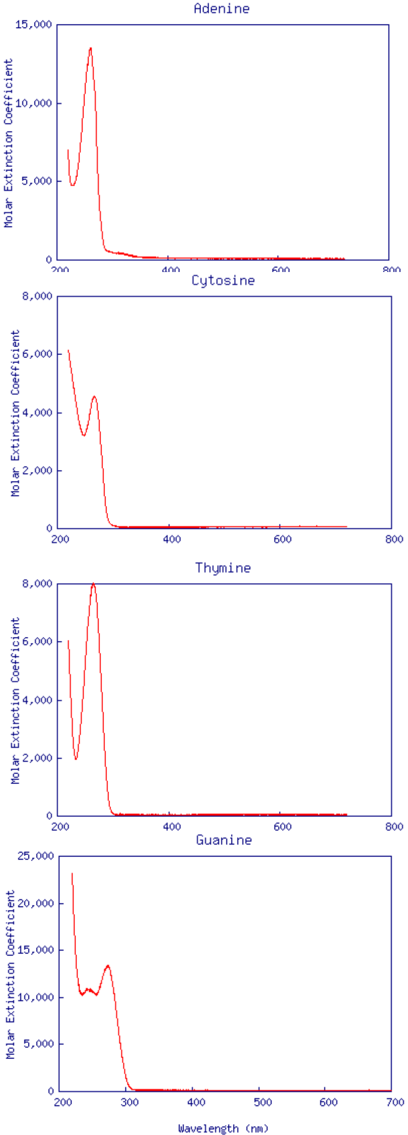


Sugar- and phosphate units

Cyclobutane pyrimidinedimer (CPD) 70-80%

Pyrimidin-Pyrimidon-Photo product (64PP) 20-30%

11. Photochem. Methods of Water Treatment

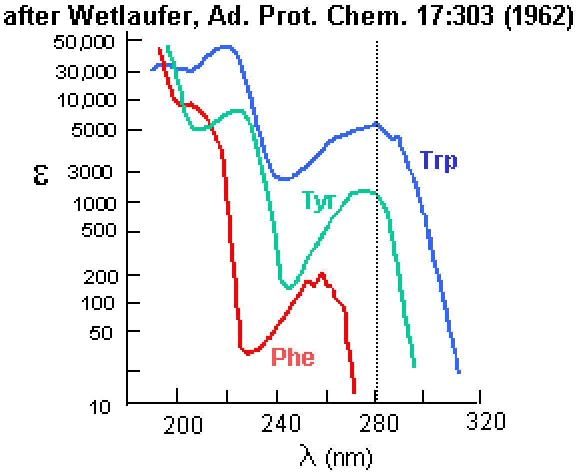


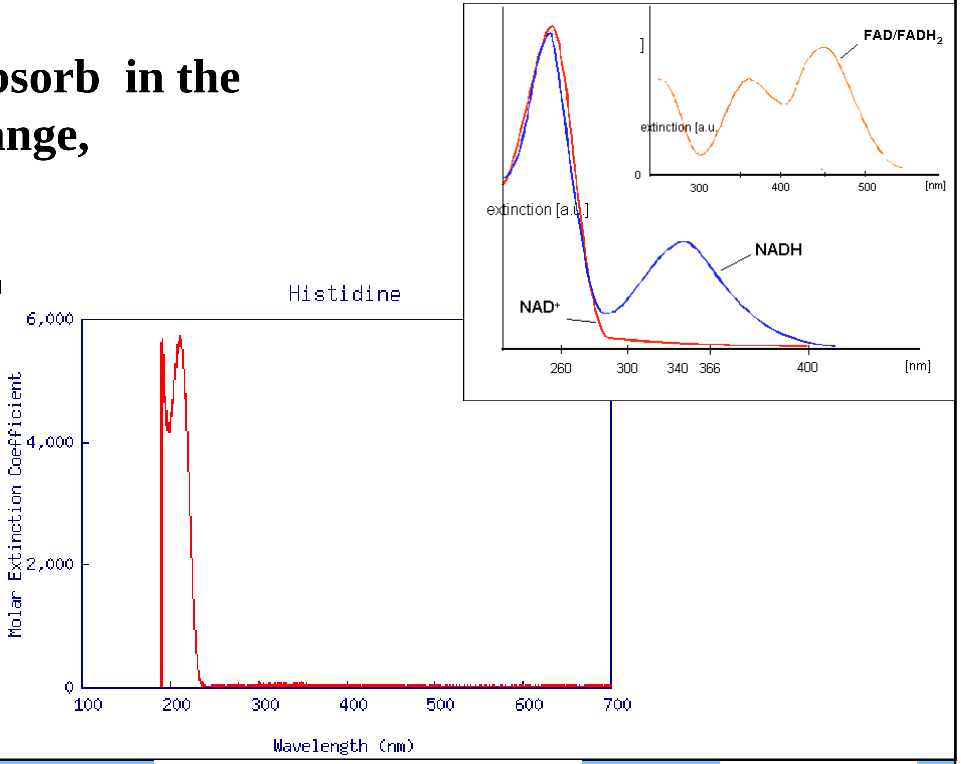
UV-Radiation - Effect on Biochemical Molecules

Nucleotides exhibit strong absorption bands at 265 nm (A, C, T, G) and at 240 nm (G) on

Aromatic amino acids show absorption bands at 280 nm (Trp, Tyr), at 250 nm (Phe) or at 210 nm (His)

Other biomolecules even absorb in the near UV or blue spectral range, e.g. NAD(P)H or $FADH_2$


after Wetlaufer, Ad. Prot. Chem. 17:303 (1962)



11. Photochem. Methods of Water Treatment

UV-Radiation - Effect on Biochemical Molecules

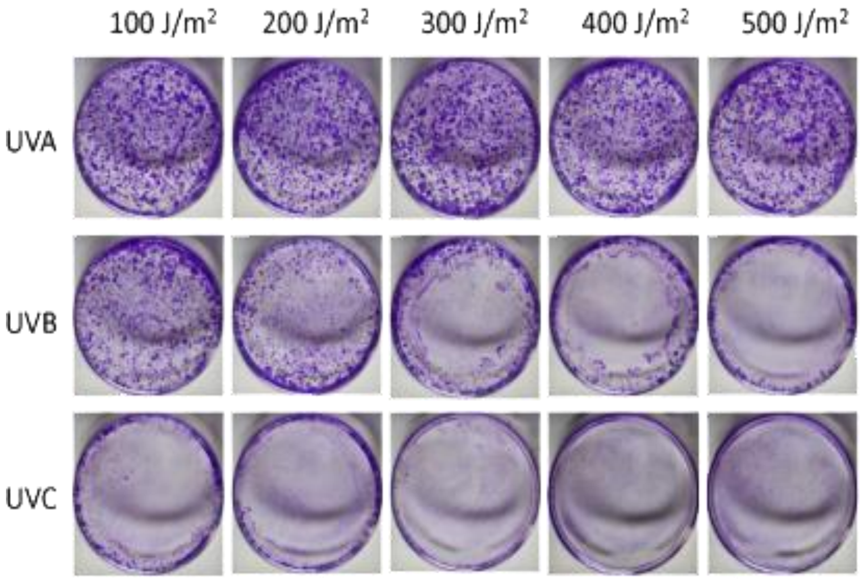
Biomolecule (chromophore)	Strongest absorption in the Band	Wavelength range
● Nucleic acids	UV-C	at 265 nm
● Proteins	UV-B	270 – 280 nm
● Urocanic acid	UV-B/A	305 – 365 nm
● Porphyrins, Haemoproteins, Cytochrome	blue green red	400 – 450 nm 500 – 560 nm 600 – 650 nm
● Flavine	blue	420 – 450 nm
● Carotenoids, Bilirubin	blue	450 – 460 nm
● Melanin	UV, VIS	300 – 700 nm
● Water	IR-A, IR-B	1400 – 1900 nm

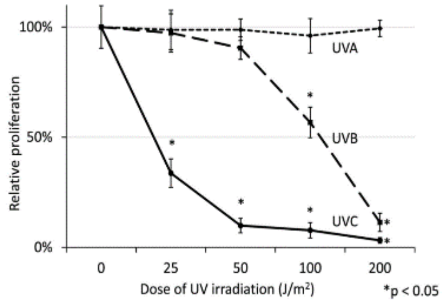
11. Photochem. Methods of Water Treatment

UV-Radiation - Effect on Microorganisms: UV-C > UV-B > UV-A


Ctrl

UV-A	**320 – 400 nm**
UV-B	**280 – 320 nm**
UV-C	**200 – 280 nm**





	Penetration characteristic	Damage conferred
UV-C	Penetrates cell membranes/cell walls	mainly DNA damage
UV-B	Most responsible for sunburns. Penetrates deeper than UV-C, but is typically adsorbed by the skin's stratum corneum (dead cell layer)	DNA and other cell components by generation of free radicals
UV-A	Long wavelengths that reach inner strata of skin causing premature aging in humans	Shown to cause membrane damage

↓ increasing penetration

lit.: S. Miwa, et. al., Journal of Cellular Biochemistry 2013, 114, 2493-2499

11. Photochem. Methods of Water Treatment

Homogeneous Catalysis in Aqueous Solution

a) VUV + Water (via bandgap)

$H_2O + h\nu \rightarrow H^{\cdot} + OH^{\cdot}$

b) UV + Hydrogen peroxide

$H_2O_2 + h\nu \rightarrow 2\,OH^{\cdot}$

c) UV + Ozone

$O_3 + h\nu \rightarrow O_2 + O^{\cdot}$

$O^{\cdot} + H_2O \rightarrow [OH^{\cdot} + {}^{\cdot}OH] \rightarrow H_2O_2$

$H_2O_2 + h\nu \rightarrow 2\,OH^{\cdot}$

d) UV/Vis + Fe^{n+} (Photo-Fenton reaction)

$Fe^{3+} + H_2O \rightarrow Fe^{2+} + H^+ + HO\cdot$

Oxidizer	Oxidation potential [V vs. NHE]
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygene	2.42
Ozone	2.07
Hydrogene peroxide	1.78
Perhydroxy radical	1.70
Hypobromic acid	1.68
Chlor dioxide	1.57
Hypochloric acid	1.49
Chlorine	1.36

Heterogeneous catalysis on semiconductor surfaces

$TiO_2 + h\nu(\text{UV-A}) \rightarrow TiO_2(h^+VB + e^-LB)$ „ Anatase phase“

$h^+VB + H_2O \rightarrow H^+ + OH^{\cdot}$ (Hydroxyl radicals)

$e^-LB + O_2 \rightarrow O_2^{\cdot -}$ (Superoxide/hyperoxide radicals)

11. Photochem. Methods of Water Treatment

Photocatalytic Degradation of Micropollutants: Mineralisation

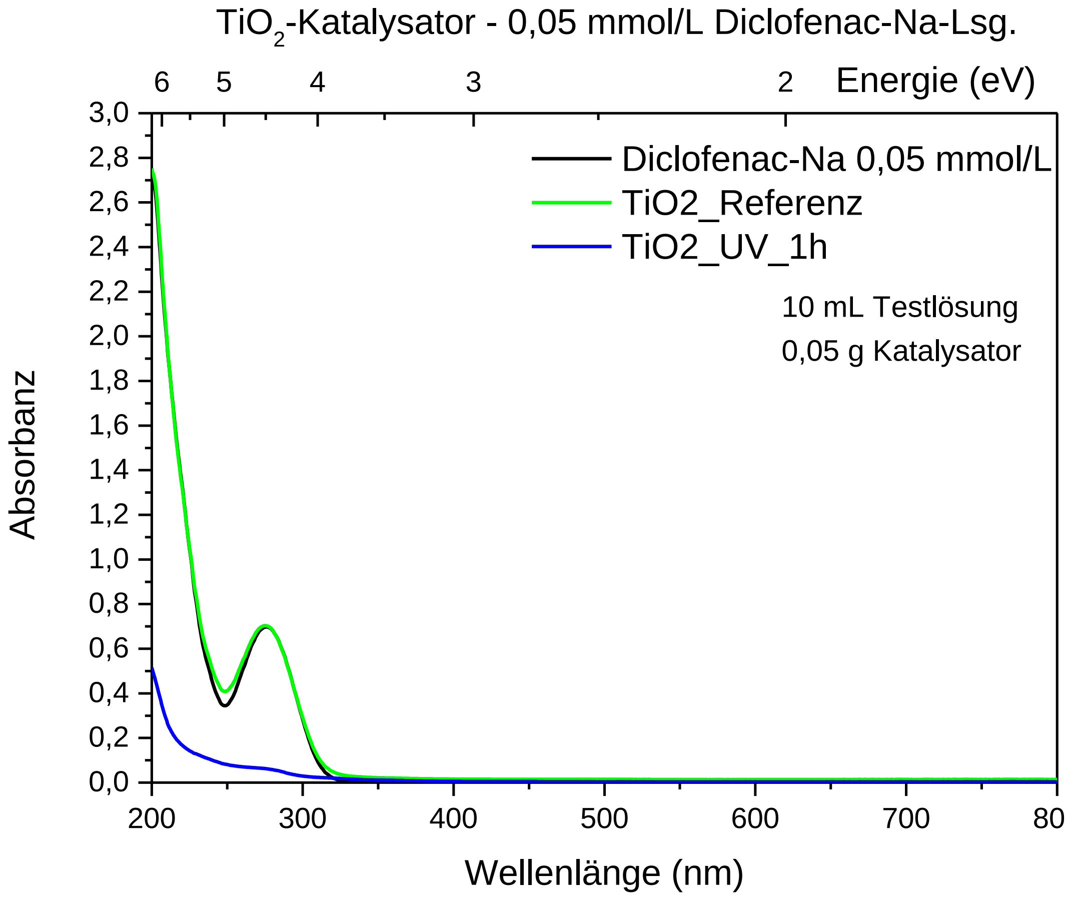
Established photocatalyst : TiO_2(Anatase)

TiO_2(Anatase) + hν → e^- + h^+

→ Degradation of diclofenac after about one hour of UV irradiation (Hg amalgam lamp)

Other photochemically Degradable micropollutants:

- **Ibuprofen**
- **Paracetamol**
- **Sulfamethoxazole**
- **Tetracyclin**
- **Trimethoprim**
- **…..**



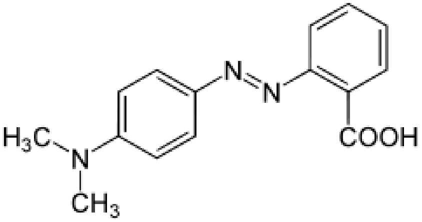
11. Photochem. Methods of Water Treatment

Photocatalytic Degradation of Micropollutants

TiO_2(Anatase) + hν → $e^- + h^+$

$e^- + O_2 \rightarrow O_2^-$

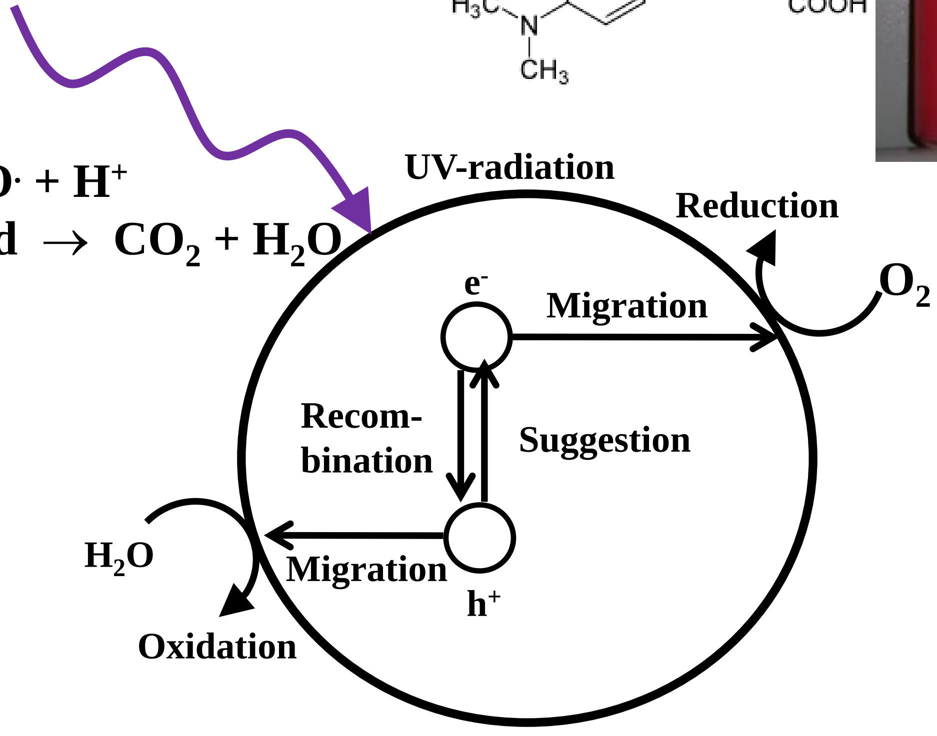
$h^+ + H_2O \rightarrow HO\cdot + H^+$
$HO\cdot$ + Methyl red → $CO_2 + H_2O$



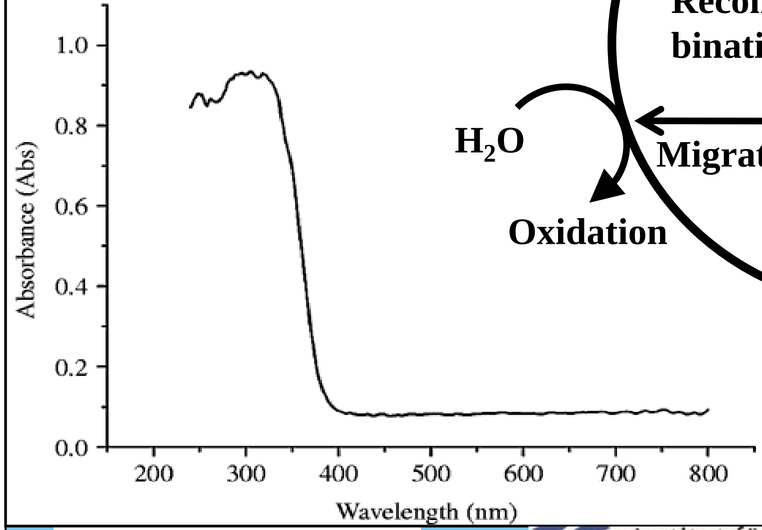

Start


After about 2 min


After about 6 min



TiO_2 Particle

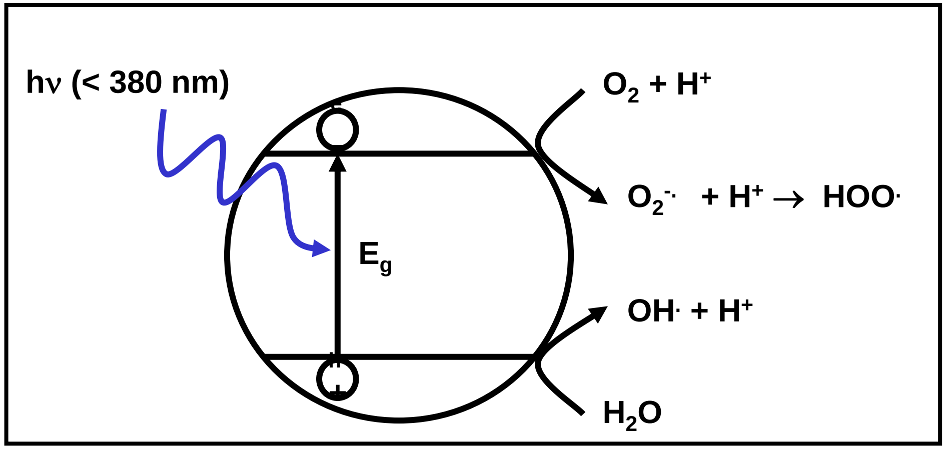


Source: Korean Journal of Chemical Engineering, January 2008, Volume 25, Issue 1, pp 64-72

11. Photochem. Methods of Water Treatment

Formation of H_2O_2 in Water

on TiO_2(Anatase) surfaces
by UV-radiation



Target reaction $2\ HOO\cdot \rightarrow H_2O_2 + O_2$ (Disproportionation)
Competitive reaction $HOO\cdot + h^+(VB) \rightarrow O_2 + H^+$

Strategies to minimize the conversion of hydroperoxy radicals into H_2O_2 to accelerate, are

a) $HOO\cdot + Cu^+ + H^+ \rightarrow H_2O_2 + Cu^{2+}$
$Cu^{2+} + e^-(LB) \rightarrow Cu^+$

b) $HOO\cdot + Mn^{2+} + H^+ \rightarrow H_2O_2 + Mn^{3+}$
$Mn^{3+} + e^-(LB) \rightarrow Mn^{2+}$

c) Incorporation of ÜM-Ionen, e.g. Fe^{3+}, in TiO_2 to capture holes

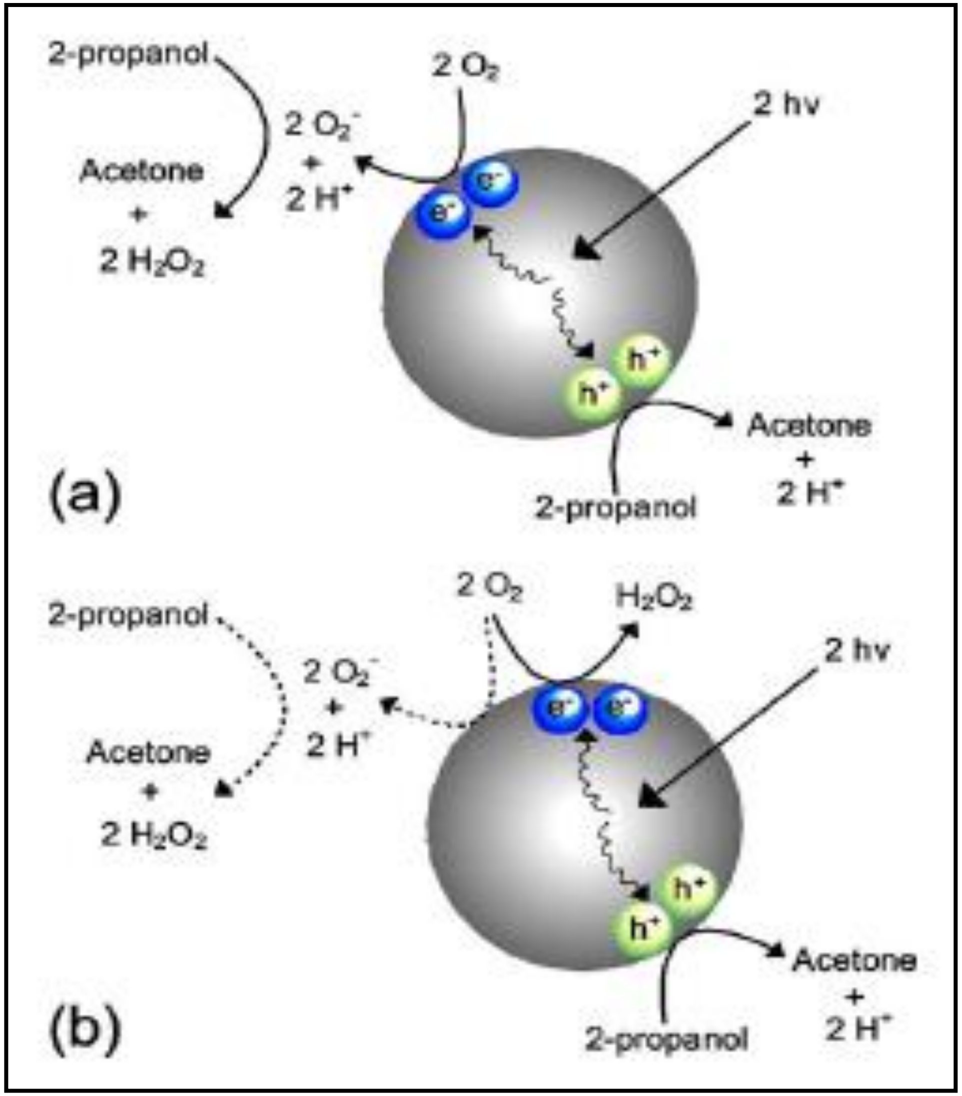
11. Photochem. Methods of Water Treatment

Formation of H_2O_2 on TiO_2 Surfaces

Influence of the TiO_2 Polymorphism

a) Rutile
Main product: Superoxide anions

b) Anatase
Main product: H_2O_2



11. Photochem. Methods of Water Treatment

Photocatalytic Degradation of Micropollutants via the Formation of OH-Radicals

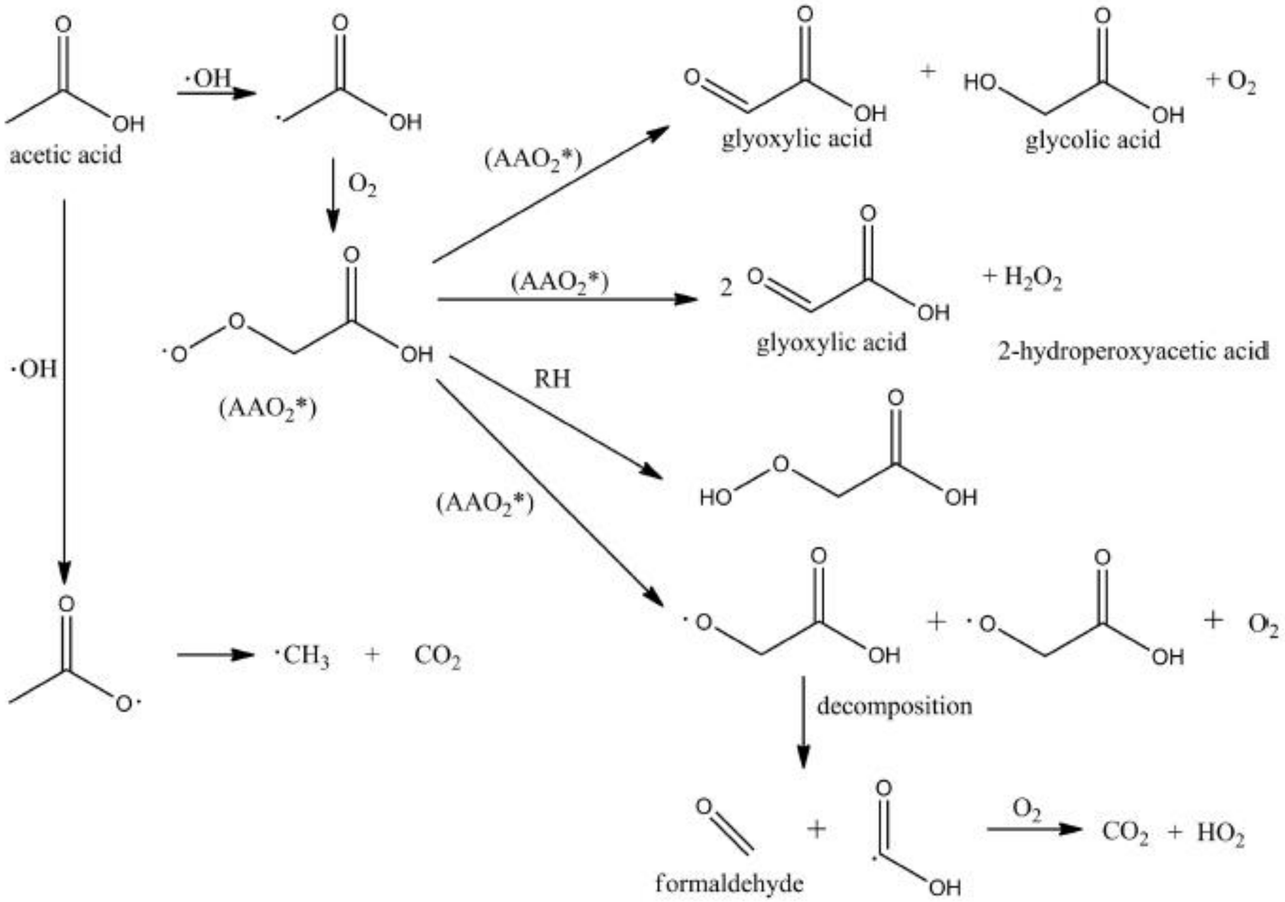
• $H_2O_2 \rightarrow {}^{\cdot}OH + {}^{\cdot}OH$	Quantum yield = 1
• $H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$	$v = 1.66 \times 10^{-11}$ cm³/s
• ${}^{\cdot}O^- + H_2O_2 \rightarrow {}^{\cdot}O_2^- + H_2O$	$v = 8.31 \times 10^{-13}$ cm³/s
• $H_2O_2 + O_3^- \rightarrow O_2 + {}^{\cdot}O_2^- + H_2O$	$v = 2.66 \times 10^{-15}$ cm³/s

• $H^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2$	$v = 3.00 \times 10^{-11}$ cm³/s
• ${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2$	$v = 9.00 \times 10^{-12}$ cm³/s
• $HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$	$v = 1.88 \times 10^{-15}$ cm³/s

Lit.: Zvereva, G.N.: Optics and spectroscopy, Vol. 108, No. 6, pp. 963-970, 2010

11. Photochem. Methods of Water Treatment

Photocatalytic Degradation of Acetate via OH-Radicals



Scheme 1. Oxidation of acetic acid by OH radical (Leitner and Dore, 1997).

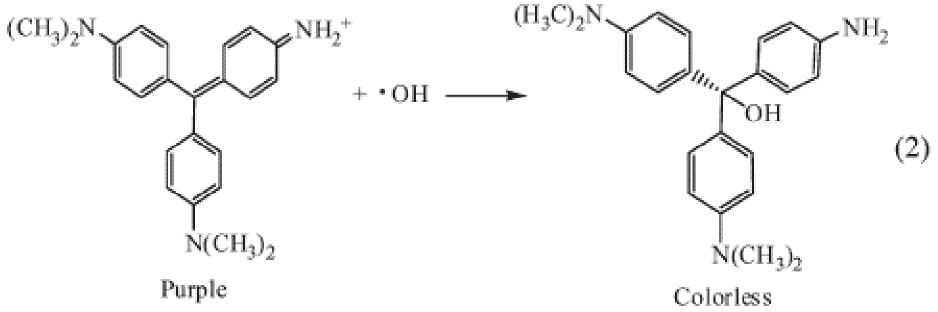
11. Photochem. Methods of Water Treatment

Photocatalytic Decolourisation of Methyl-Violet via OH-Radicals

Hydroxyl radicals add electrophilically to methyl violet (MV)

The violet MV is thereby into a colourless product

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \qquad (1)$$



- **NaN_3 acts as a quencher for hydroxyl radicals, protecting MV from electrophilic attack**
- **$2\ Na^+ + 2\ N_3^- + 2\ {}^{\bullet}OH \rightarrow 2\ Na^+ + 2\ OH^- + 3\ N_2\uparrow$ UV-VUV Degradation**

Lit.: Ying Xue: J. Phys. Chem. C 2011, 115, 4433-4438

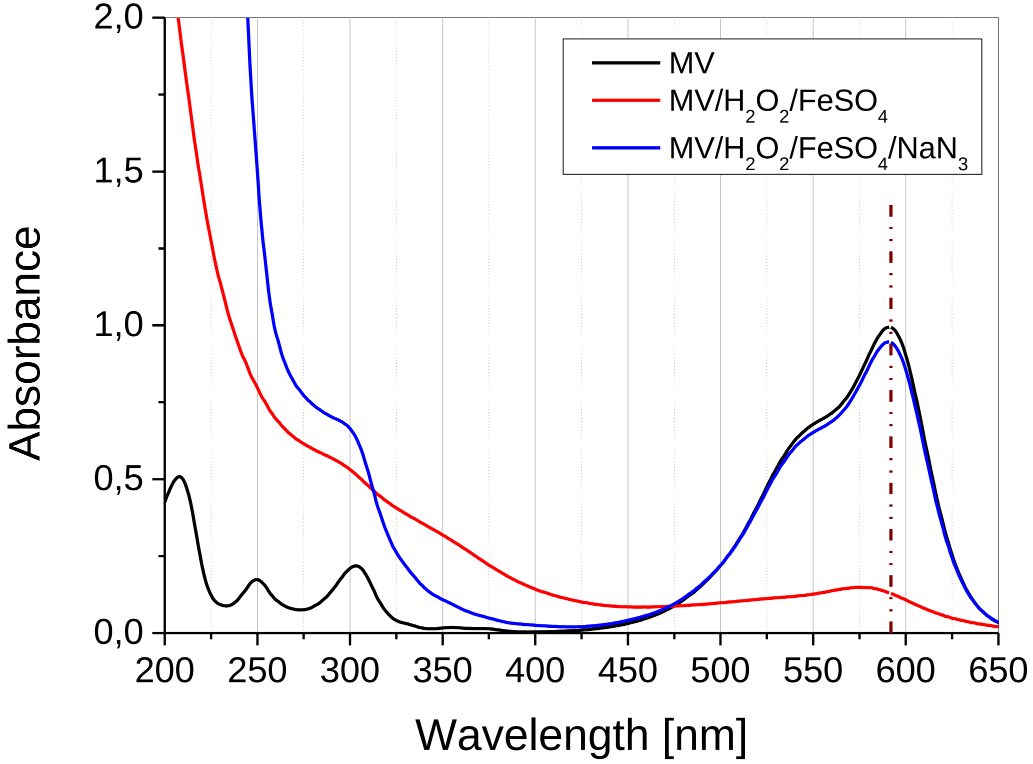
11. Photochem. Methods of Water Treatment

Degradation of Methyl-Violet (MV)

If Fe^{2+} is added to an MV/H_2O_2 solution, the Fenton reaction is initiated, which produces hydroxyl radicals that attack MV electrophilically

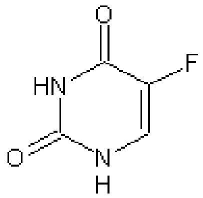
The addition of NaN_3 prevents the degradationreaction of MV by •OH is prevented

→ Azide is also a "Quencher"!

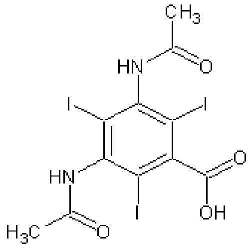


11. Photochem. Methods of Water Treatment

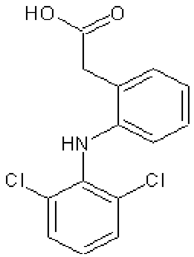
Some Critical Pharmaceuticals



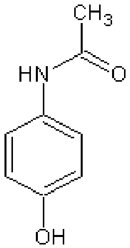
5-Fluorouracil – Cytostatic agent



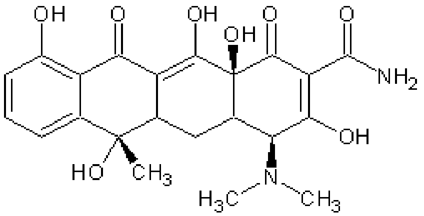
Natriumamidotrizoat – X-ray contrast agent



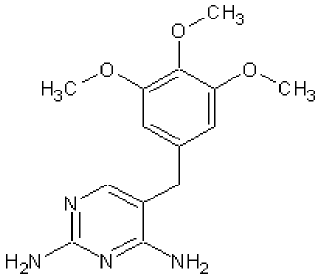
Diclofenac – Analgesic



Paracetamol – Analgesic



Tetracyclin – Antibiotic



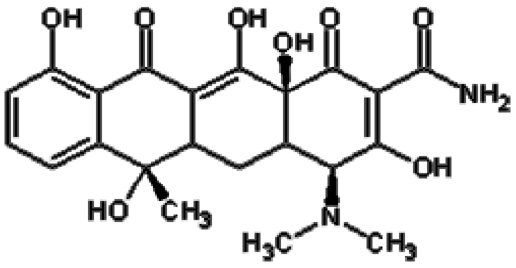
Trimethoprim – Antibiotic

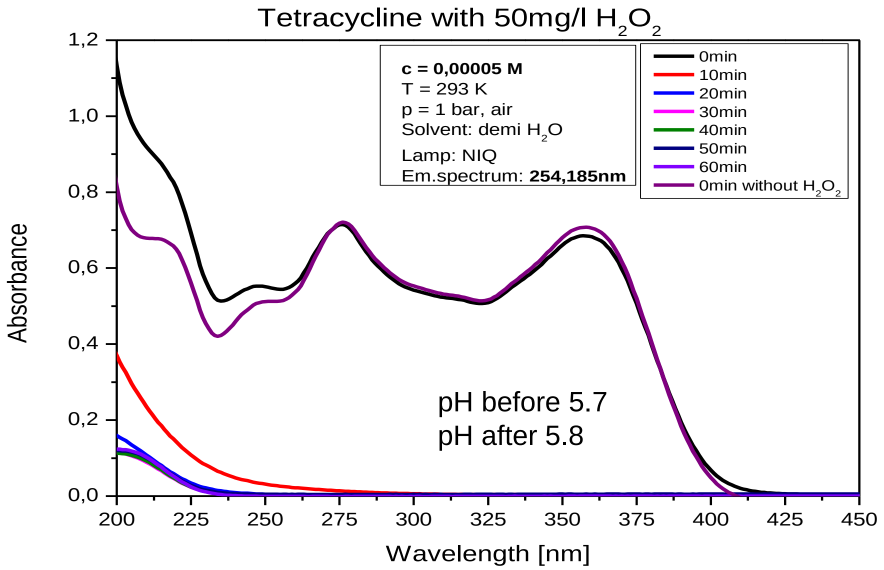
State Connection	Germany 2000	Germany 2001	Austria 1997	England 2000	Switzerland 2004	Australia 1998	Denmark 1997	France 1999
Paracetamol [t/year]	641.86	621.65	35.08	390.9	95.20	295.9	0.24	2294

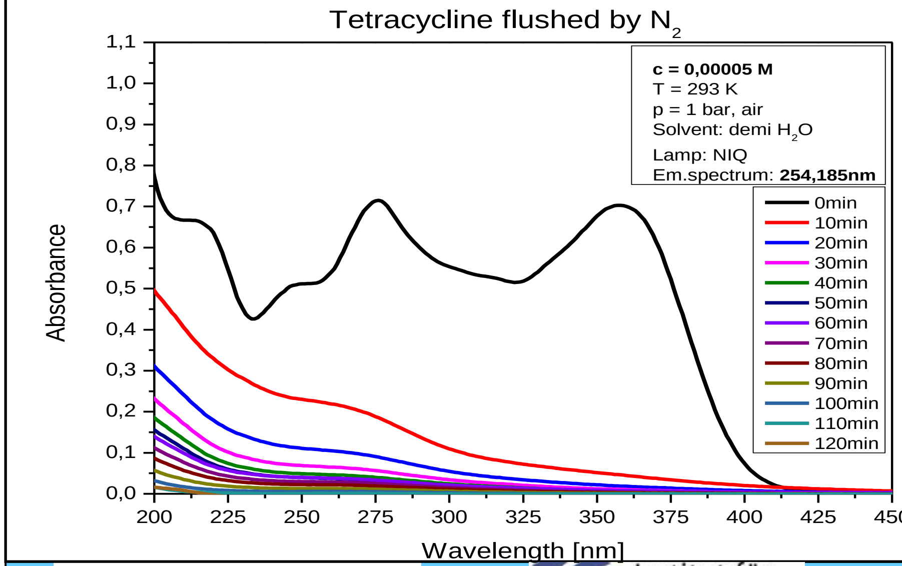
11. Photochem. Methods of Water Treatment

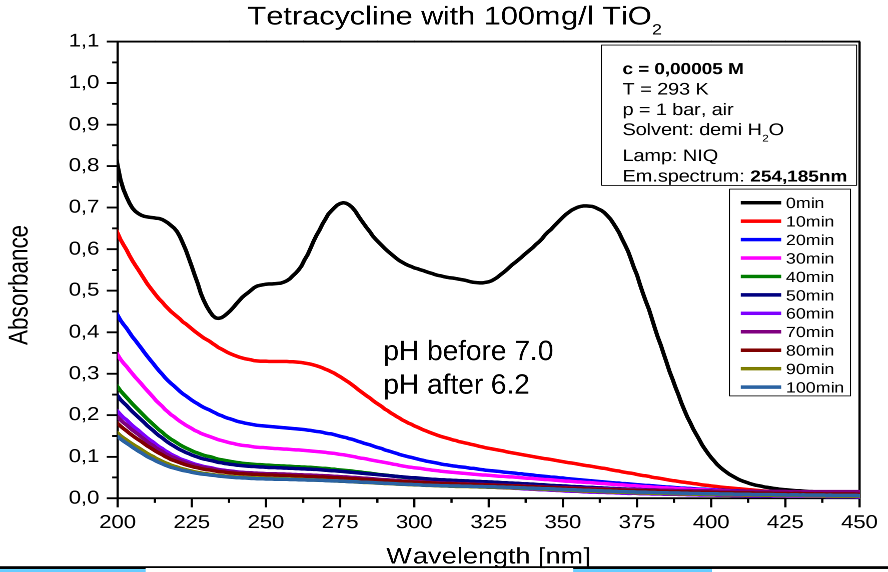
Photodegradation of Micropollutants

Results for Tetracycline




Tetracycline with 50mg/l H_2O_2


Tetracycline flushed by N_2


Tetracycline with 100mg/l TiO_2

11. Photochem. Methods of Water Treatment

Areas of Application

Drinking water

- Communal
- Private households (Point of use POU, Point of entry POE)
- Swimming and wellness pools
- Ships, boats

Process water

- Food and beverage industry
- Pharmaceutical industry
- “Personal Care” Products (e.g. cosmetics)
- Semiconductor and microelectronics industry
- Aquariums
- Aquacultures and fish farms

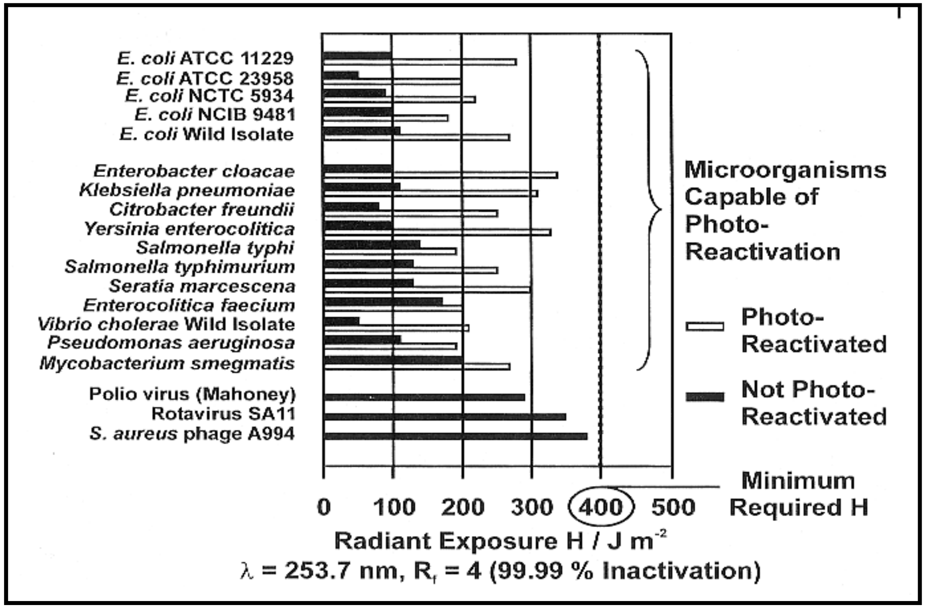
Waste water

- Communal
- Industry
- Hospitals, clinics

11. Photochem. Methods of Water Treatment

Standards and Regulations

- NSF/ANSI Standard 55 (USA)
  - Class A (Safety level): 40 mWs/cm^2
  - Class B (Suppl.): 16 mWs/cm^2
- DVGW (BRD)
  - 400 J/m^2 (254 nm)
  - Verification with test organisms (E. coli, B. subtilis)
  - Reduction of 99.99% = log 4



Some influencing factors

- Water flow / water quality (turbidity, absorption strength)
- Reactor design
- Lamp ageing / efficiency
- „Fouling „ of the cover, sleeve
- Type of microorganisms (radiation sensitivity, photoreactivation, etc....)

11. Photochem. Methods of Water Treatment

Type of Microorganisms

Radiation resistance

Resistance

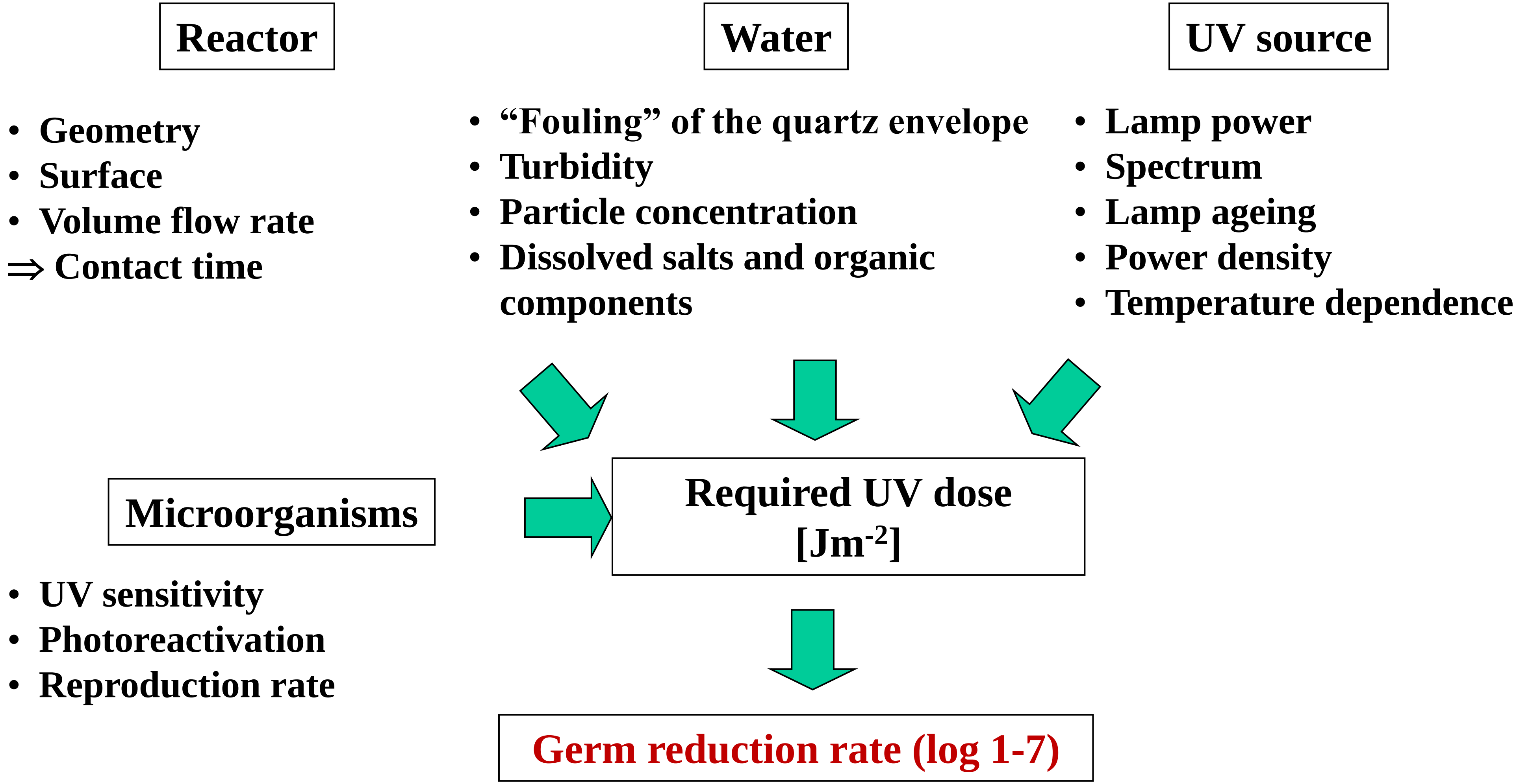
- Vegetative bacteria: Salmonella, E. coli, etc.: Low
- Enteroviruses: coliphages, HAV, norovirus : Moderate
- Bacterial spores
- Fungal spores
- Protozoa, (Oo)cysts, spores, worm eggs, etc.
  - Cryptosporidium parvum Oocysts
  - Giardia lamblia cysts
  - Ascaris lumbricoides eggs
  - Acid-resistant bacteria: Mycobacterium spp.
- Biofilms

High

Increase

11. Photochem. Methods of Water Treatment

Overview of Factors Influencing Disinfection Efficiency



Reactor

- Geometry
- Surface
- Volume flow rate

⇒ Contact time

Water

- “Fouling” of the quartz envelope
- Turbidity
- Particle concentration
- Dissolved salts and organic components

UV source

- Lamp power
- Spectrum
- Lamp ageing
- Power density
- Temperature dependence

Microorganisms

- UV sensitivity
- Photoreactivation
- Reproduction rate

Required UV dose [Jm^{-2}]

Germ reduction rate (log 1-7)

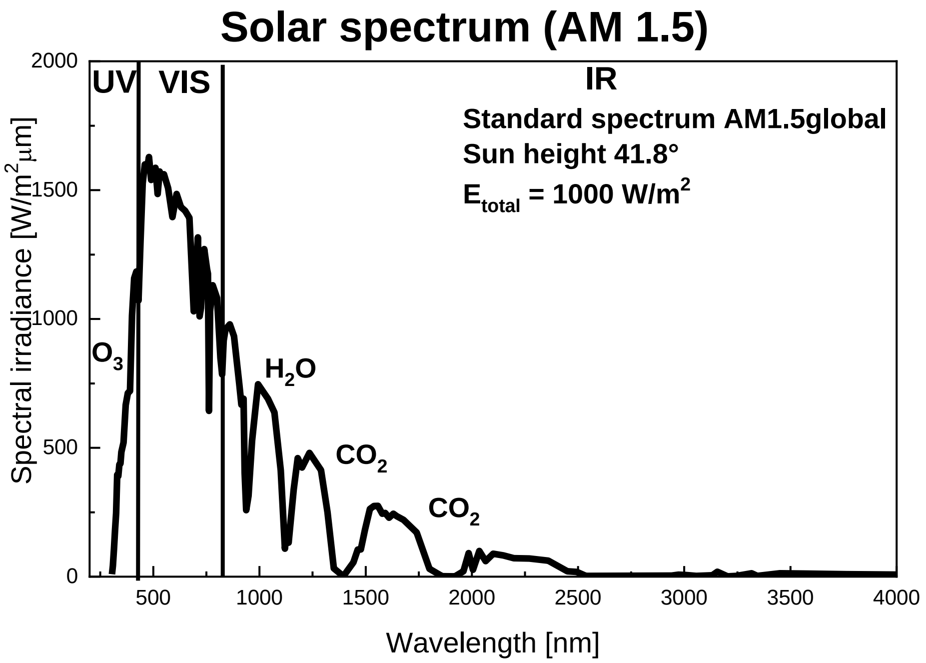
11. Photochem. Methods of Water Treatment

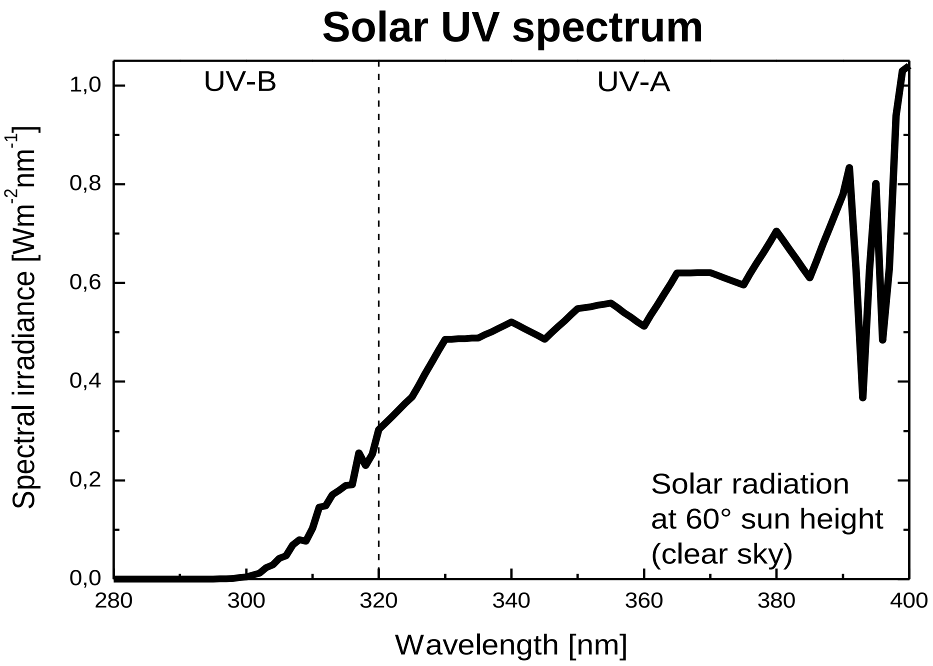
UV Radiation Sources

Sun	> 300 nm
Hg-Vapour lamps	
- Low pressure	185, 254 nm
- Amalgam	185, 254 nm
- Medium pressure	200 – 400 nm
Xe/(Hg)- Discharge lamps	230 – 800 nm
D_2- Discharge lamps	110 – 400 nm
Excimer-Laser	
- ArF*	193 nm
Excimerlamps (Dielectrically hindered discharge: DHD)	
- Xe_2*	172 nm (+ Fluorescent material: Fluorescent DBE)
- KrCl*	222 nm
- XeBr*	282 nm
- XeCl*	308 nm
(Al,Ga)N LEDs	205 – 365 nm (+Fluores.mat.:phosphor converted LEDs)
(Al,Ga)N Laser diodes	205 – 365 nm
X-rays or cathode rays + phosphor	200 – 400 nm

11. Photochem. Methods of Water Treatment

Solar Radiation (Solar Constant ~ 1000 W/m², ~ 3% UV, < 0.1% UV-B)





UV irradiance ~ 30 W/m²

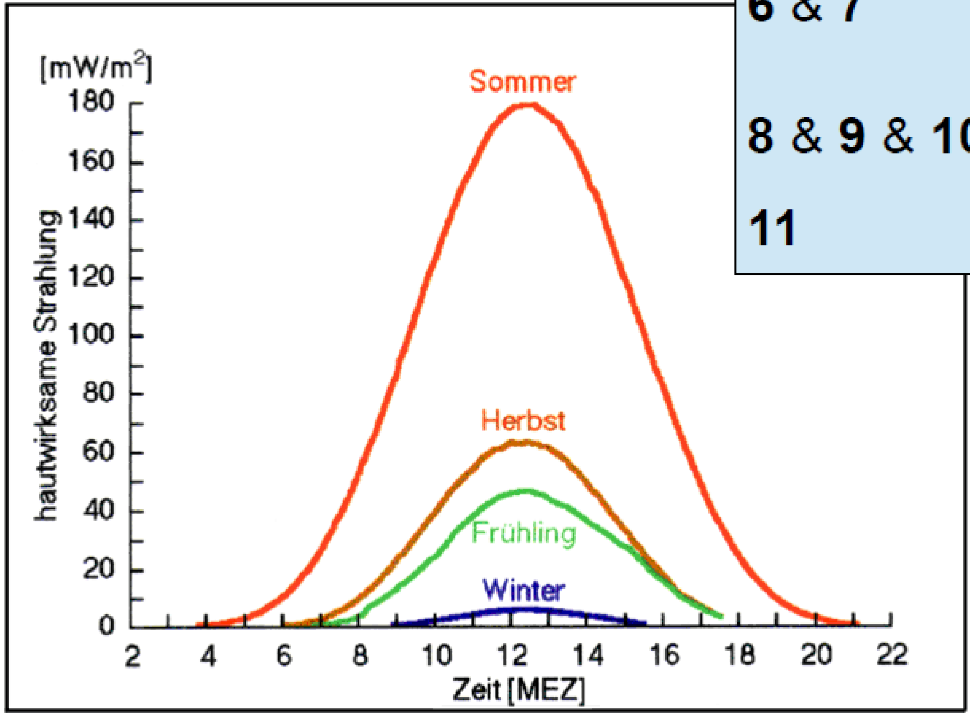
Depending on latitude, time of day, time of year, altitude above sea level and atmospheric conditions (aerosol concentration, dust, humidity, etc. , …)

11. Photochem. Methods of Water Treatment

Solar Radiation (Solar Constant ~ 1000 W/m², ~ 3% UV, < 0.1% UV-B)

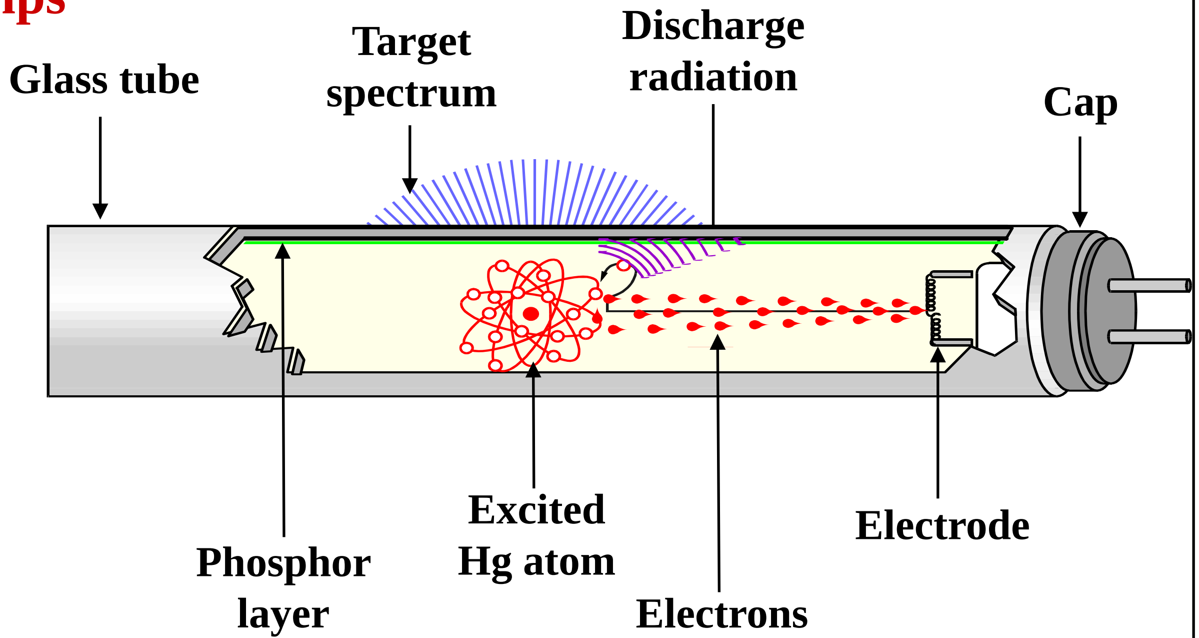
Seasonal progression

UV-Index	Bestrahlungs-stärke [W/m2]	Stärke	Notwendiger Schutz
1 & 2	0.05 (UVI: 2)	**Schwach**	Kein Schutz erforderlich
	0.125 (UVI: 5)	**Mittel**	Hut, T-Shirt, Sonnenbrille, Sonnencreme
6 & 7	0.175 (UVI: 7)	**Hoch**	Hut, T-Shirt, Sonnenbrille, Sonnencreme
8 & 9 & 10	0.25 (UVI: 10)	**Sehr hoch**	Aufenthalt im Freien möglichst vermeiden
11	0.275 (UVI: 11)	**Extrem**	Aufenthalt im Freien möglichst vermeiden



11. Photochem. Methods of Water Treatment

Hg Low Pressure Discharge Lamps



Hg discharge → **UV-C radiation** $\xrightarrow{\text{Fluorescent}}$ **UV-A/B-radiation**

UV-C radiation → **Purification**
O$_3$ formation

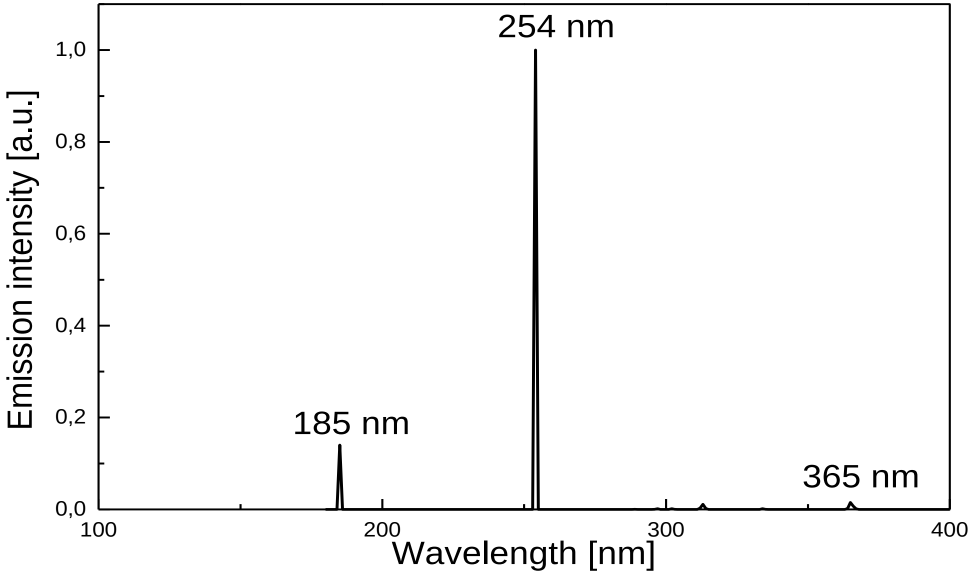
UV-C radiation → **Disinfection**

UV-A/B-radiation → **Photochemistry / Photobiology**

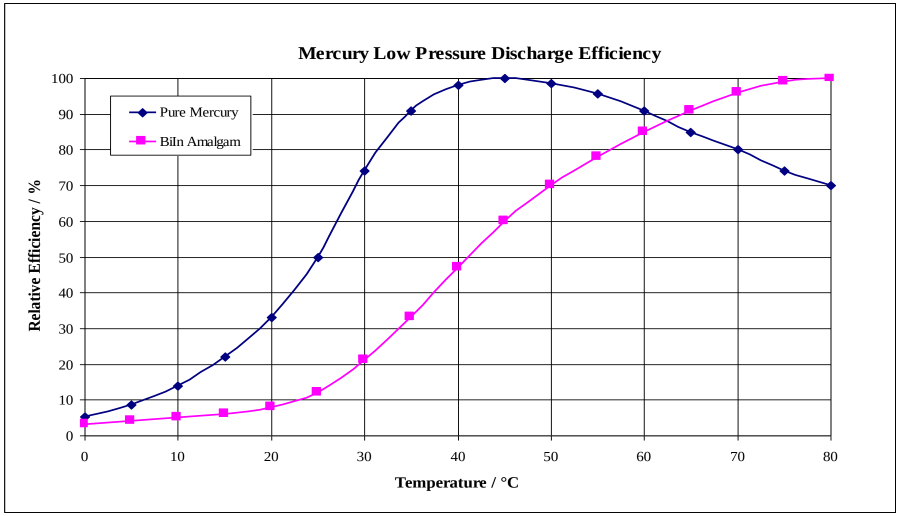
11. Photochem. Methods of Water Treatment

Hg Low Pressure Discharge Lamps

Lamp spectrum



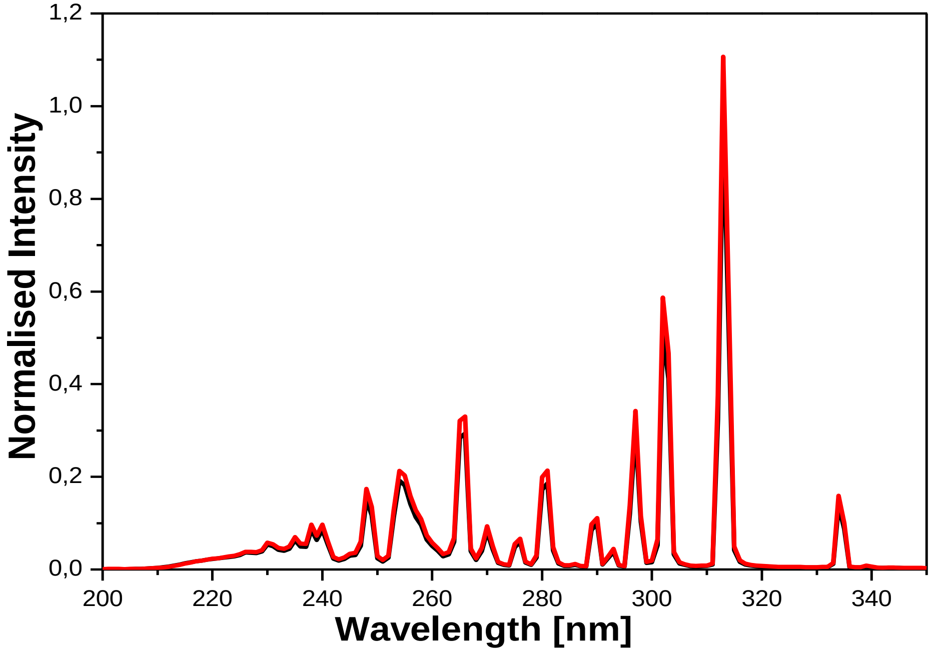
Temperature dependency



- Highest radiation yield at about 45 °C („cold spot“)
- Optimized for 25 °C ambient temperature
- 85% emission at 253.7 nm, 12% at 185.0 nm, remainder at 313, 365 nm, and several lines in the visible range: 405, 436, 546, 579 nm
- Typical service life ~ 10,000 h

11. Photochem. Methods of Water Treatment

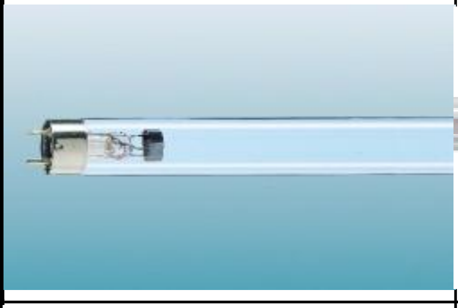
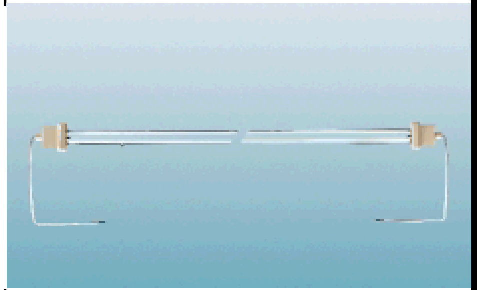
Hg Medium Pressure Discharge Lamps



- Strongest emission in the UV-A/UV-B range but more visible radiation than low-pressure lamps
- Semi-continuous spectrum in the UV-C range
- Operating temperature : 600 - 800 °C
- High power density + compact design, but lower efficiency

11. Photochem. Methods of Water Treatment

Hg Radiation Sources: Overview

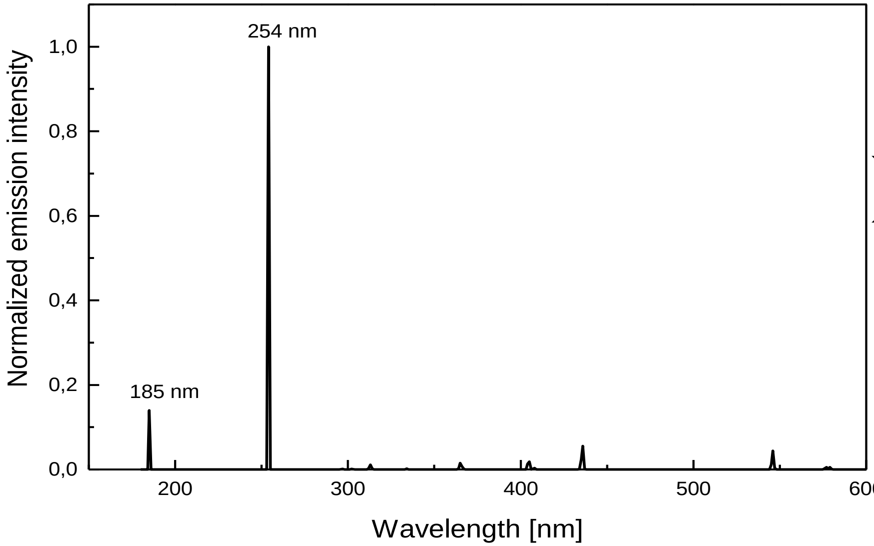
	Low-pressure-Hg	Amalgam	Medium pressure-Hg
			
Wavelength range	254 nm	254 nm	200 - 280 nm
Power consumption	4...100 W	100...300 W	1...17 kW
Efficiency	< 40%	30...35%	10...15%
GAC factor	85%	85%	80%
UV-C Power	0.2 W / cm	0.7 W / cm	15 W / cm
Wall temperature	40 °C	100 °C	600 - 900 °C

⇒ Selection depending on application and operating costs

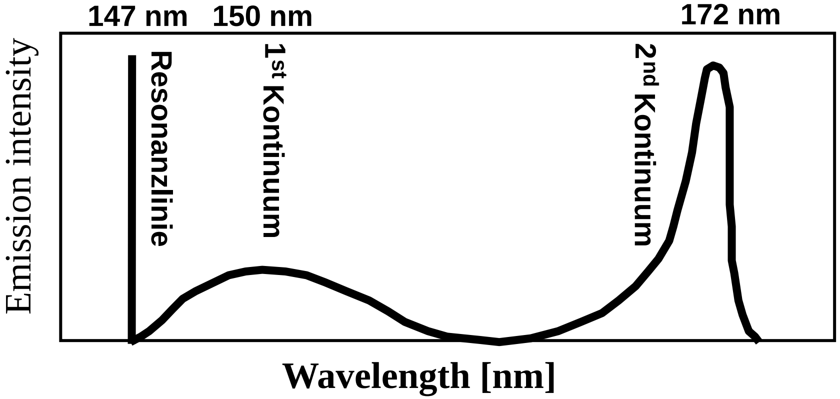
11. Photochem. Methods of Water Treatment

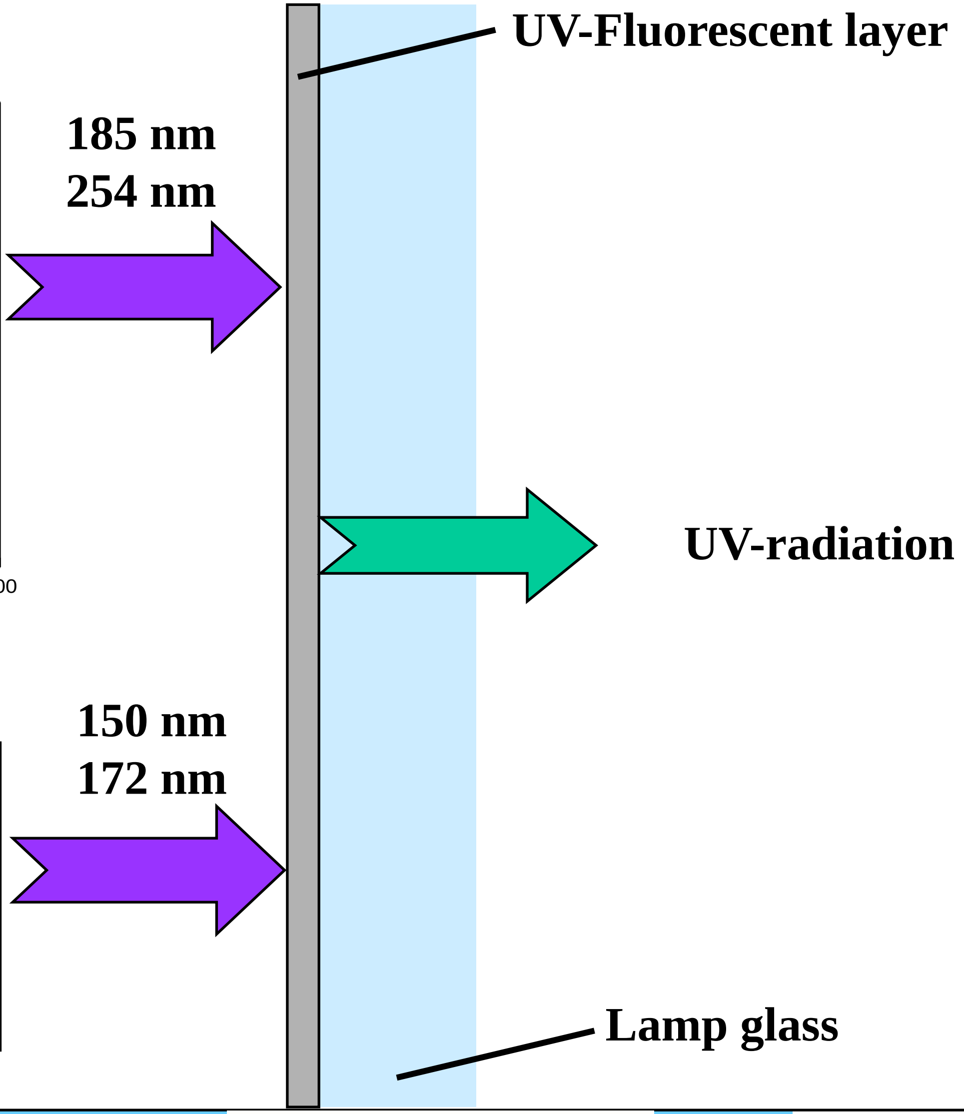
UV Fluorescent Lamps

Hg low-pressure discharge



Xe_2*- excimer discharge





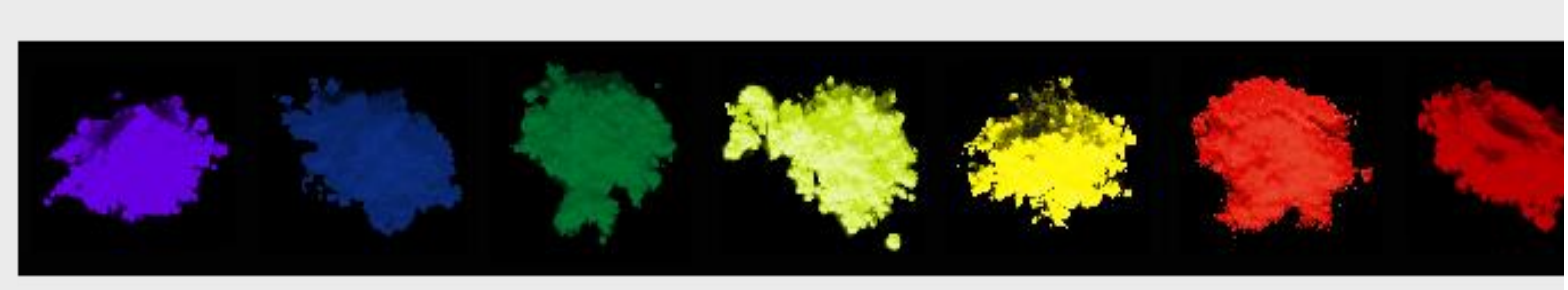
11. Photochem. Methods of Water Treatment

Definiton Phosphor (Luminescent pigment, Luminophore)

Micro- or nanoscale pigment which, after excitation by radiation (NIR, VIS, UV, X-ray, gamma), high-energy particles, by an increase in temperature or after mechanical stress such as ultrasound or pressure (visible) electromagnetic radiation in non-thermal equilibrium.

Under daylight

Upon excitation by electrons or UV radiation



11. Photochem. Methods of Water Treatment

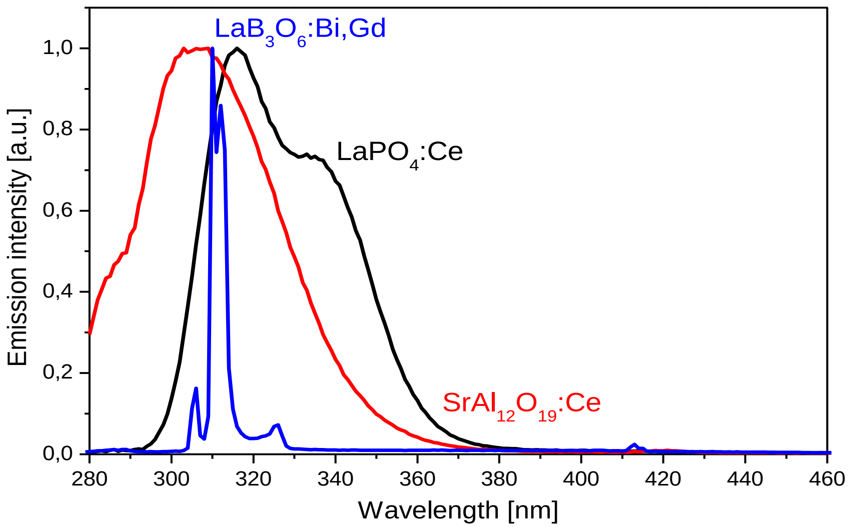
Inorganic Phosphors for Hg-Low-Pressure Discharge Lamps

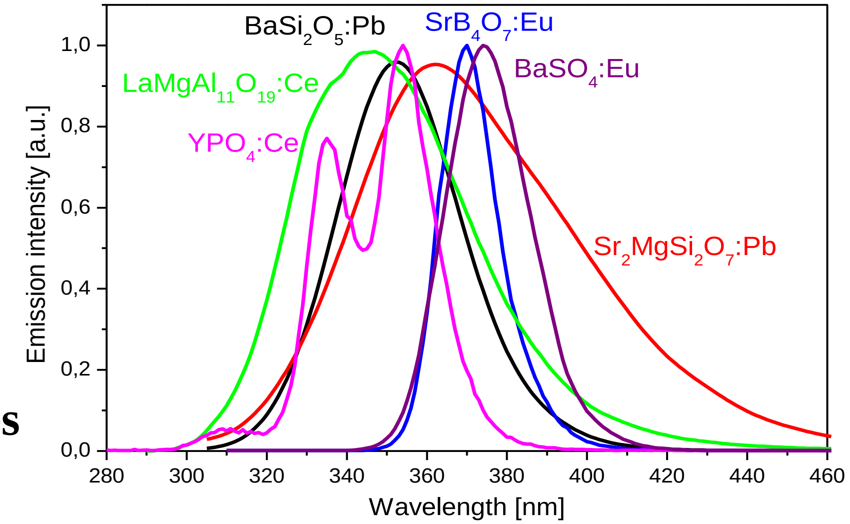
$SrAl_{12}O_{19}:Ce^{3+}$	**305 nm**
$LaB_3O_6:Bi^{3+},Gd^{3+}$	**311 nm**
$LaPO_4:Ce^{3+}$	**320 nm**

$LaMgAl_{11}O_{19}:Ce^{3+}$	**340 nm**
$(Y,Gd)PO_4:Ce^{3+}$	**335, 355 nm**
$BaSi_2O_5:Pb^{2+}$	**350 nm**
$Sr_2MgSi_2O_7:Pb^{2+}$	**365 nm**
$SrB_4O_7:Eu^{2+}$	**370 nm**
$BaSO_4:Eu^{2+}$	**375 nm**

Host lattice: borates, aluminates, phosphates, silicates

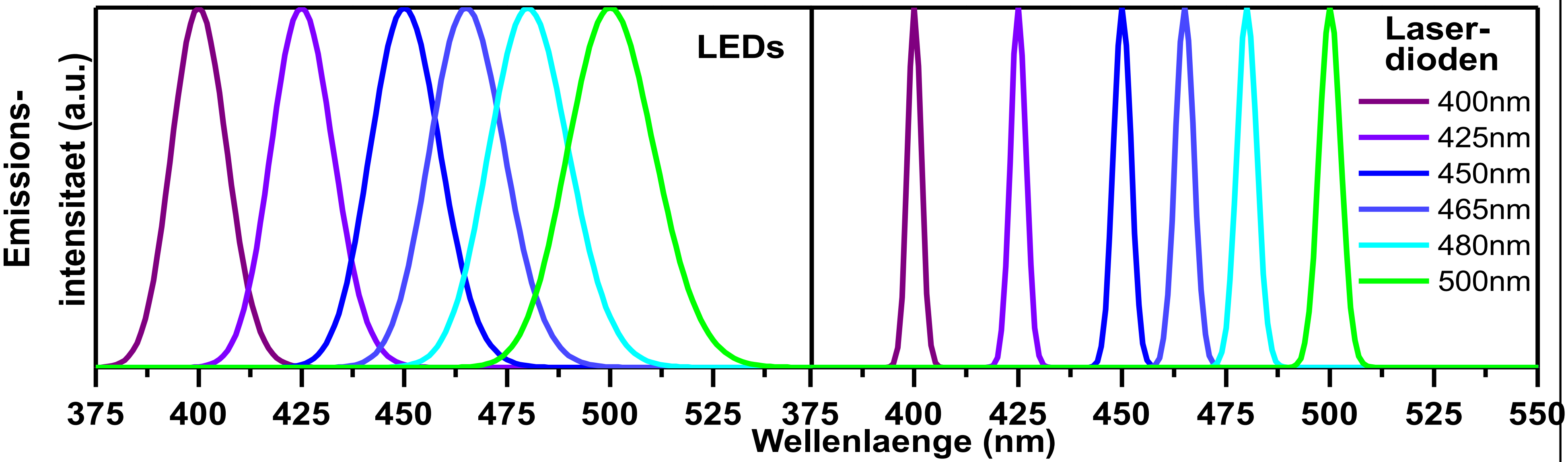
Activators: Ce^{3+}, Gd^{3+}, Pb^{2+}, Eu^{2+}





12. New Radiation Sources

LEDs and Laser Diodes



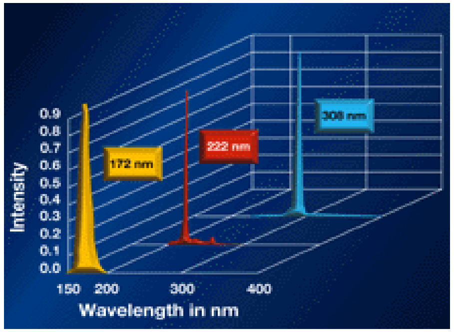
„LED platform“	
465 nm LEDs	Lighting
365 nm LEDs	Blacklight
265 nm LEDs	Disinfection

„Laser diodes platform“	
785 nm	CD
655 nm	DVD
405 nm	Blue ray DVD

12. New Radiation Sources

Excimers are Molecules that are only Stable in an Excited State

Excimer lamps are powerful UV sources, e.g. with pure xenon



$Xe + e^- \rightarrow Xe^* + e^-$

$Xe^* + Xe \rightarrow Xe_2^*$

$Xe^* + F \rightarrow XeF^*$

$Xe_2^* \rightarrow 2\,Xe + h\nu$

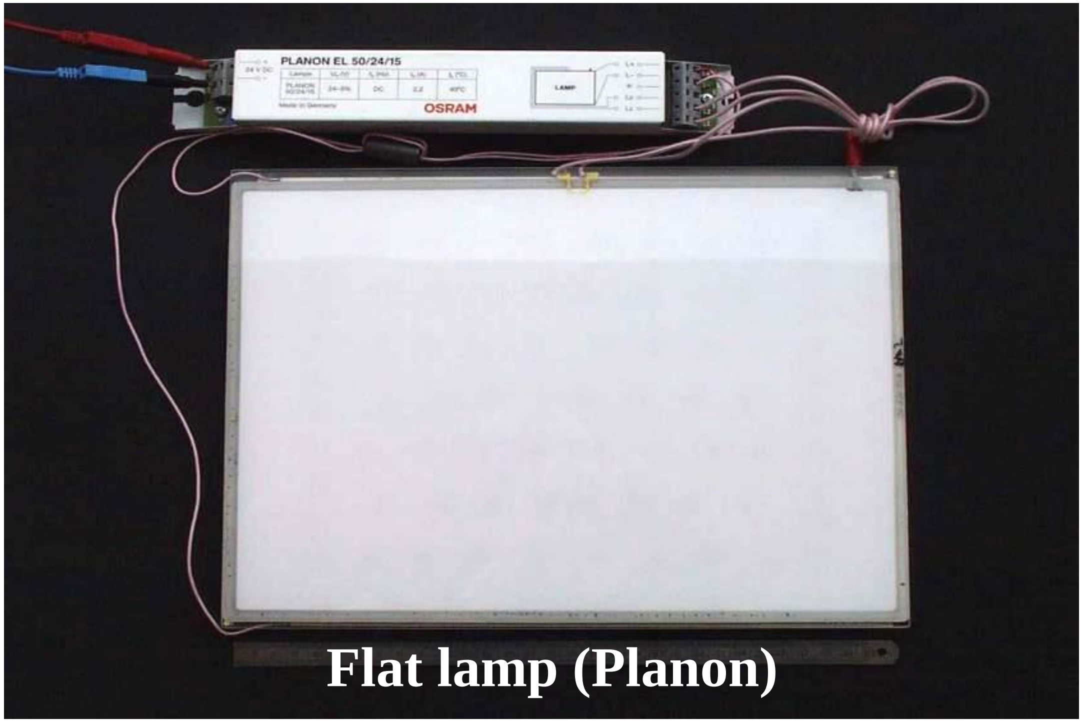
$XeF^* \rightarrow Xe + F + h\nu$

Efficiency with a sinusoidal driver (50 kHz)

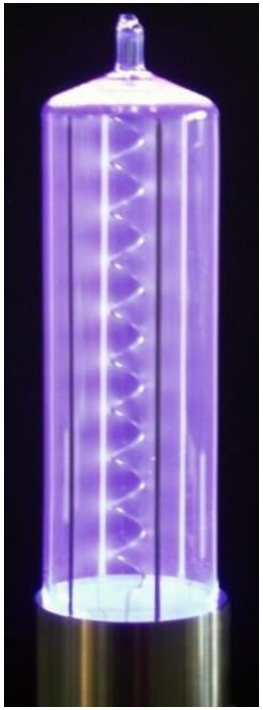
	F	Cl	Br	I	Pure noble gas
Ar	> 10 % 193 nm	ca. 5 % 175 nm	< 0.1 % 161 nm		Ar^*_2: ~10% 126 nm
Kr	> 10 % 248 nm	18 % 222 nm	ca. 5 % 207 nm	< 0.1 % 185 nm	Kr^*_2: ~15% 146 nm
Xe	> 10 % 351 nm	14 % 308 nm	15 % 282 nm	ca. 5 % 253 nm	Xe^*_2 : 30 % 172 nm

12. New Radiation Sources

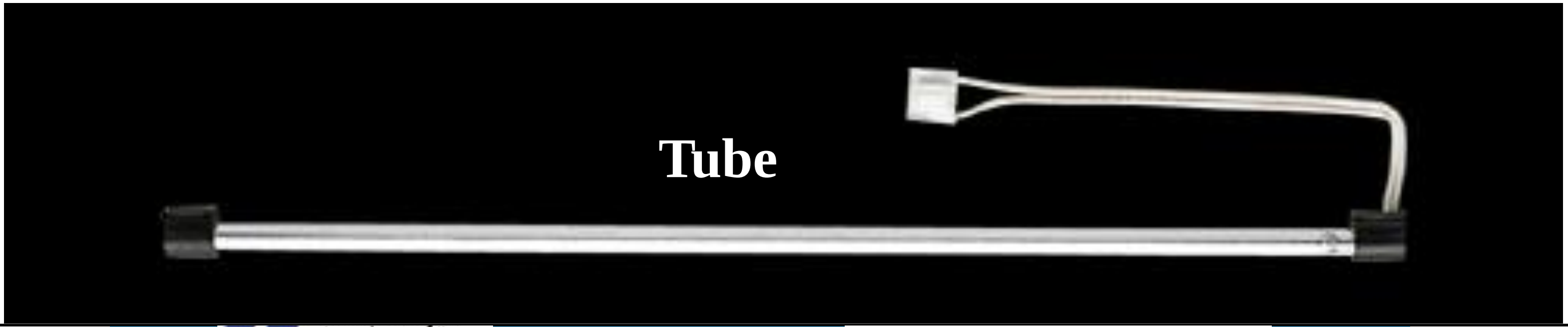
Excimer Discharge Lamps - Some Types



Flat lamp (Planon)



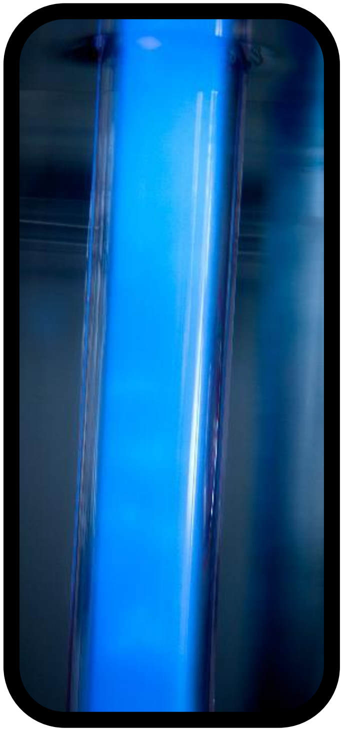
Central wire lamp

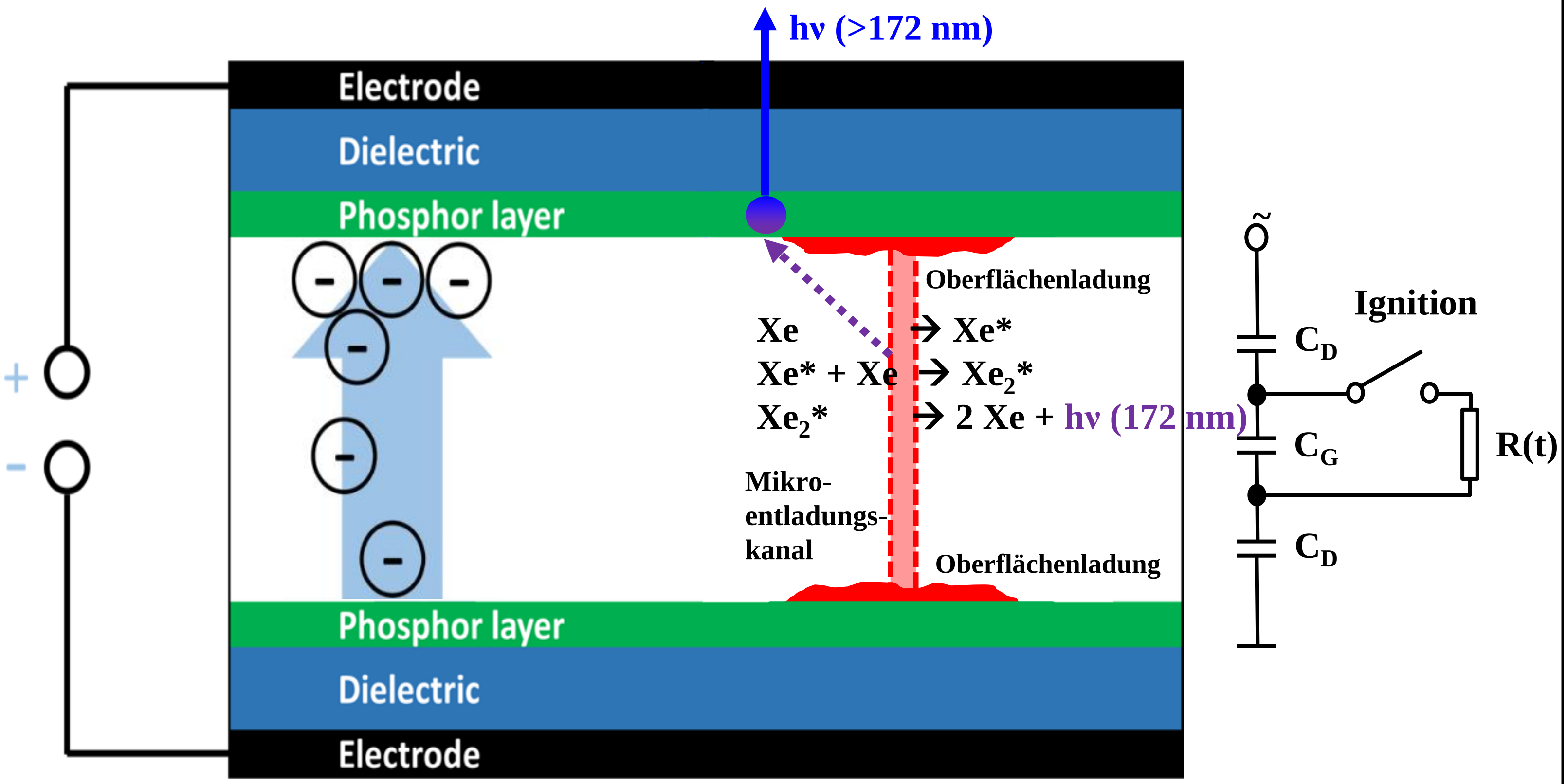


Tube

12. New Radiation Sources

Excimer Discharge Lamps - Operating Principle

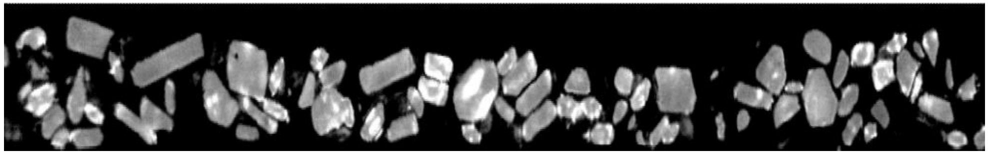




$Xe \rightarrow Xe^*$

$Xe^* + Xe \rightarrow Xe_2^*$

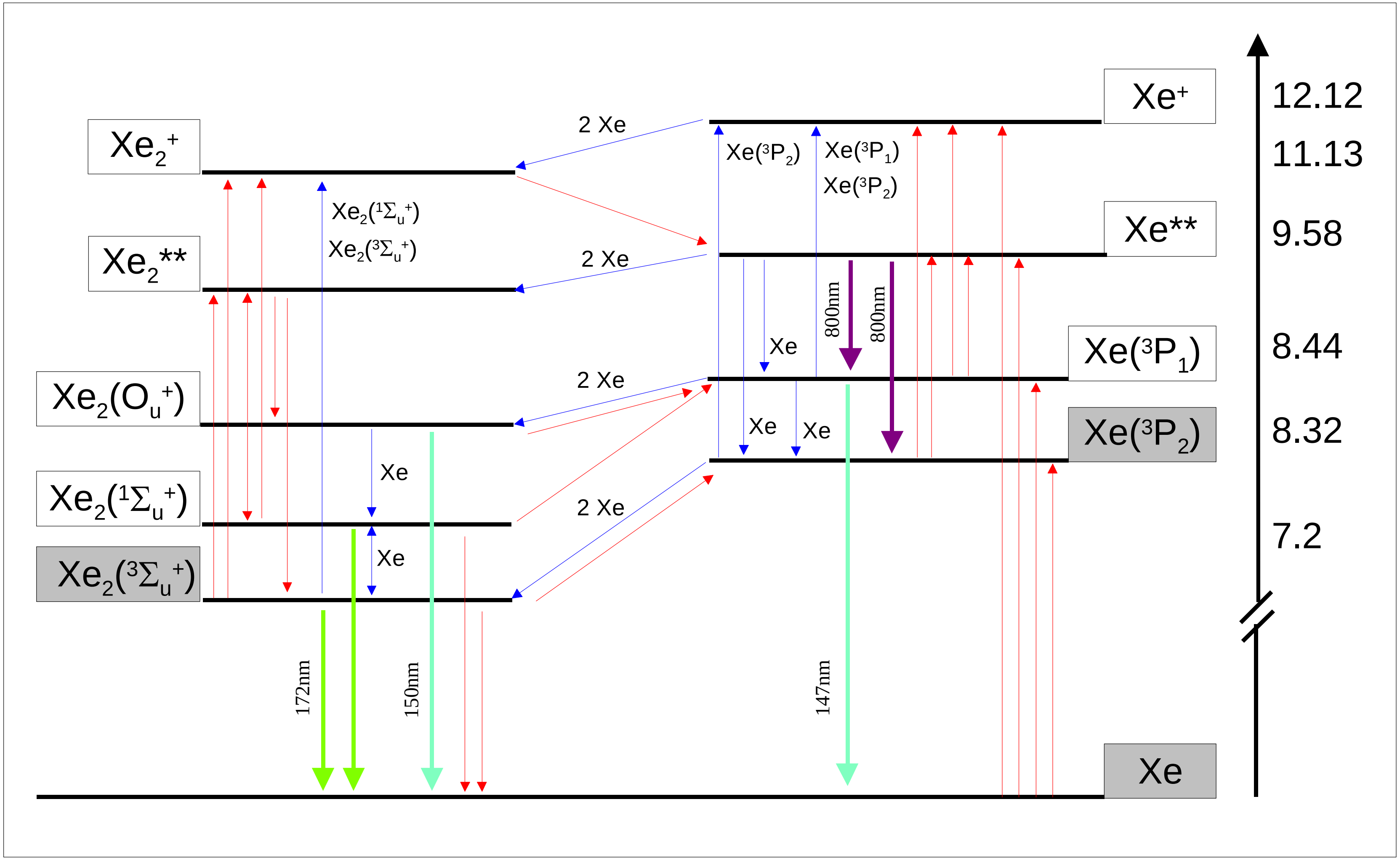
$Xe_2^* \rightarrow 2\,Xe + h\nu$ (172 nm)



YPO_4:Bi Layer (241 nm)

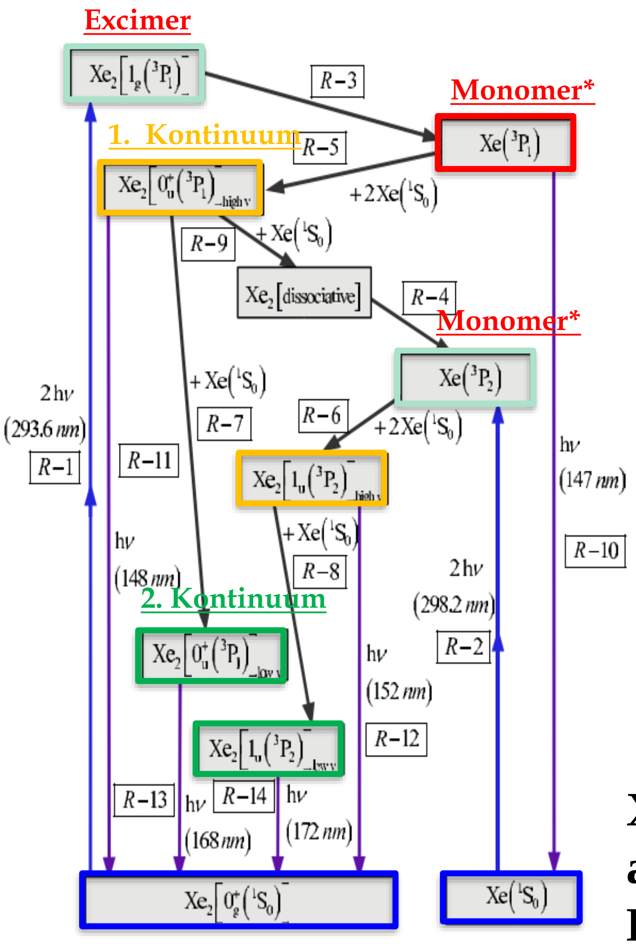
12. New Radiation Sources

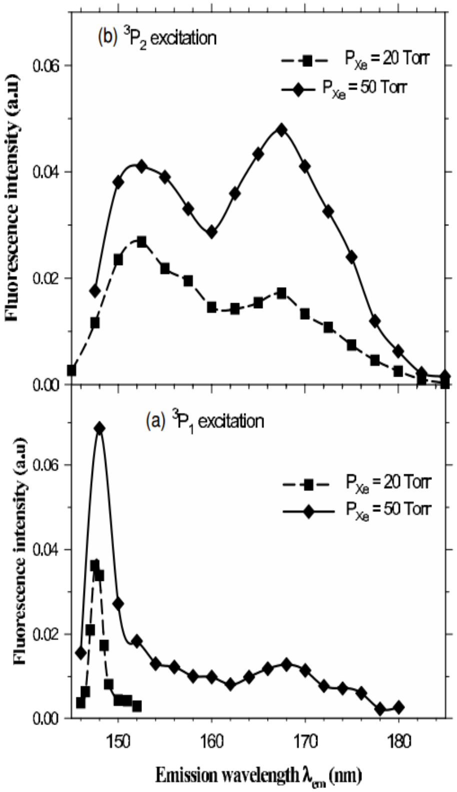
Excimer Discharge Lamps: Xe Discharge



12. New Radiation Sources

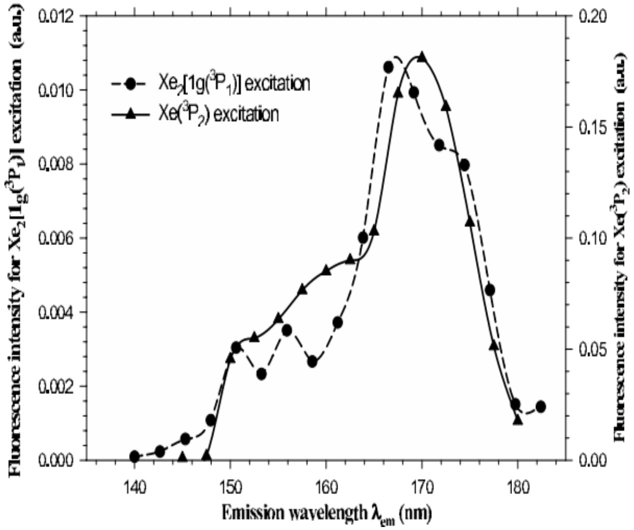
Excimer Discharge Lamps - Xe Pressure Dependence





$Xe_2[1g(^3P_1)]$ // $Xe(^3P_2)$ Excitation at 20 and 50 Torr Xe
(~ 27 mbar or 67 mbar)
Emission: 1st and 2nd continuum

The emission spectrum is strongly dependent on filling pressure

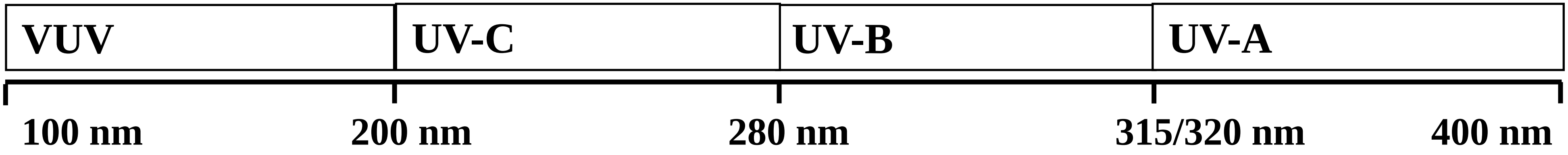


$Xe_2[1g(^3P_1)]$ // $Xe(^3P_2)$ excitation at 200 Torr Xe (~ 266 mbar)
Emission: 2nd continuum

Lit.: G. Ledru. et al. J. *Phys. B: At. Mol. Opt. Phys*. 2006, 39, 231-2057

12. New Radiation Sources

UV-Phosphors for Excimer Lamps - Suitable Materials



Host material

(Fluorides) Phosphates Borates Silicates Aluminates (Garnets)

Activators

Nd^{3+}

Sc^{3+}, Tl^{+}, Pb^{2+}, Pr^{3+}, Bi^{3+}

Gd^{3+}, Bi^{3+}, Pr^{3+}, Ce^{3+}

Tm^{3+}, Pb^{2+}, Ce^{3+}, Eu^{2+}

12. New Radiation Sources

UV-Phosphors for Excimer Lamps - Germicidal Efficiency

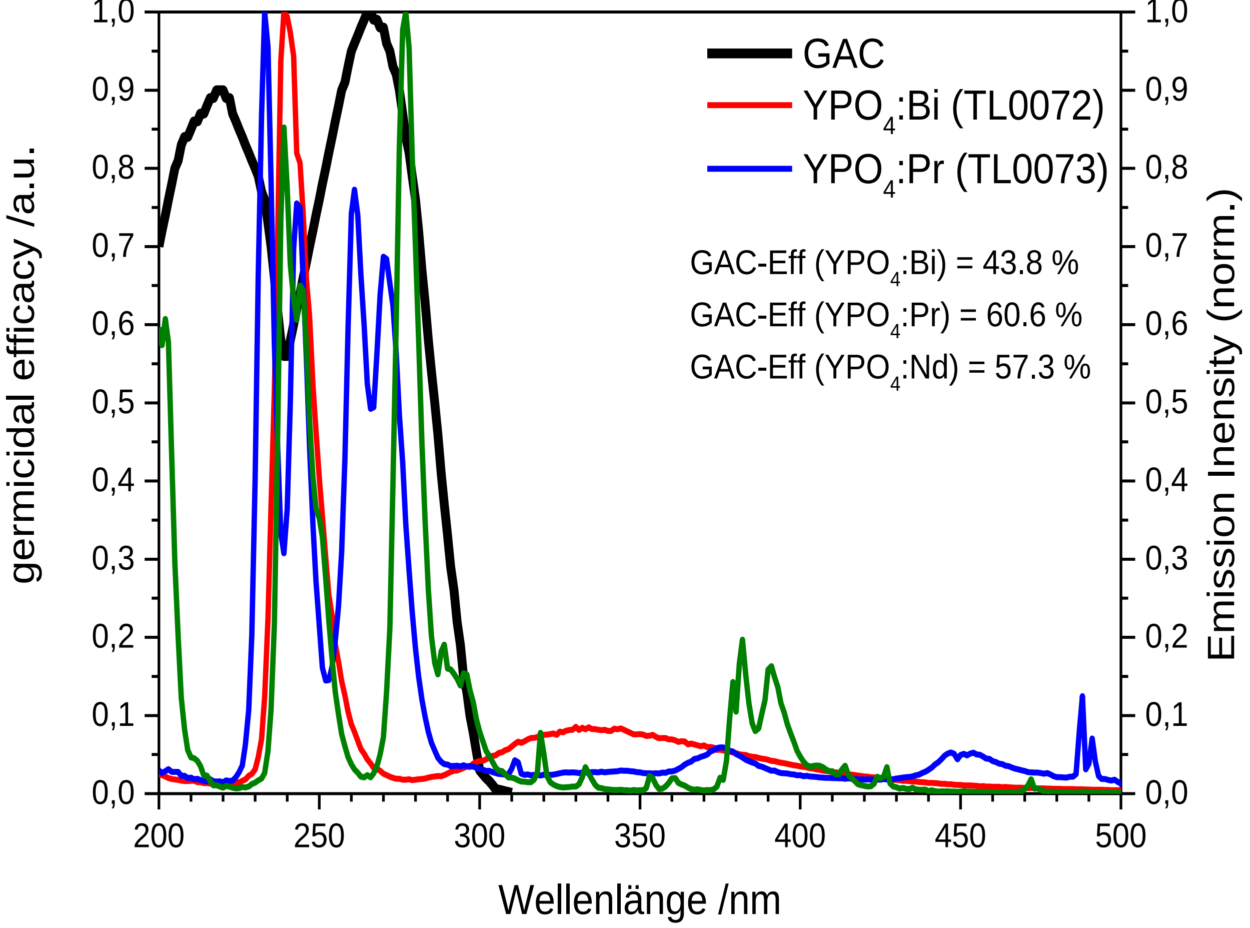
Calculation of the germicidal efficiency:

1. **Germicidal efficacy spectrum (GAC-Kurve E(λ))**

2. **Integral normalized emission spectrum S(λ)**

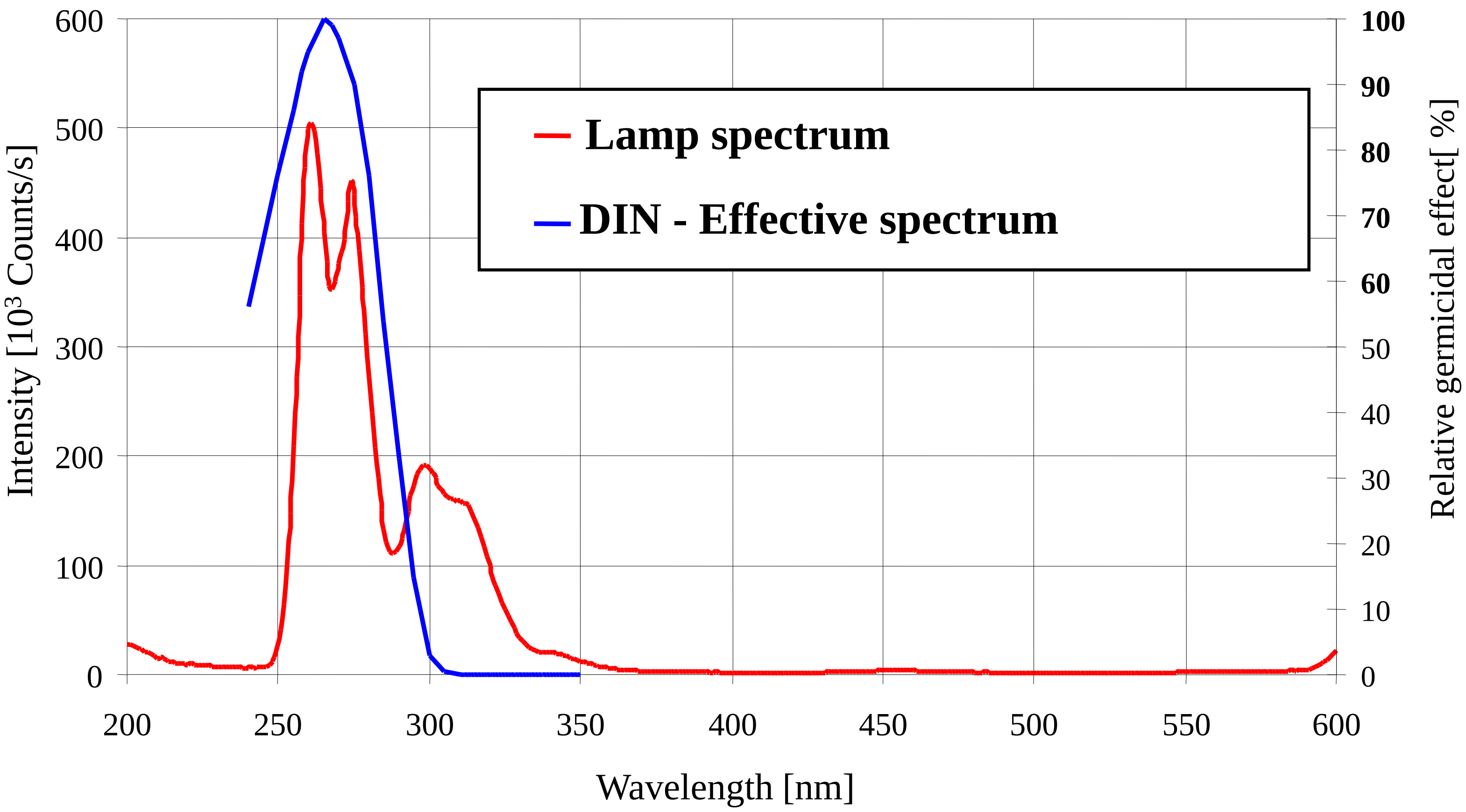
$$\int_A^B E(\lambda) * S(\lambda) d\lambda = I$$

spectral germicidal efficacy DIN 5031-10 (E.Coli)



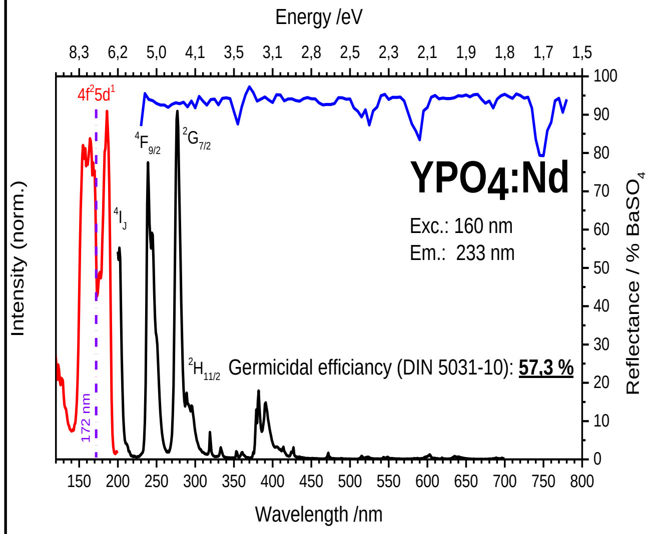
12. New Radiation Sources

Spectrum of a Xe-Excimer Lamp with YBO_3:Pr as a VUV to UV-C Converter

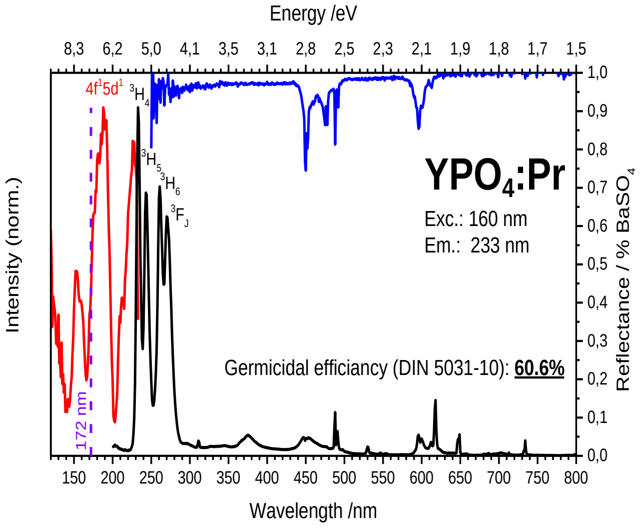


12. New Radiation Sources

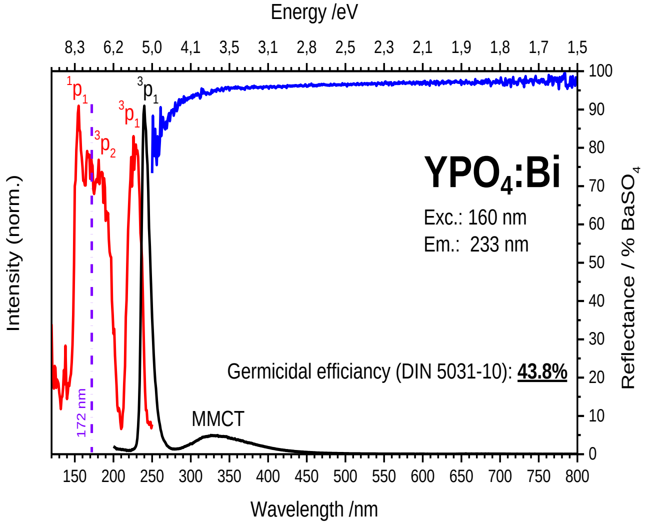
Converter for Xe Excimer Emitters: Radiation Resistant ortho-Phosphates



λ_{max}(YPO$_4$:Nd) = 192 nm



λ_{max}(YPO$_4$:Pr) = 235 nm



λ_{max}(YPO$_4$:Bi) = 241 nm

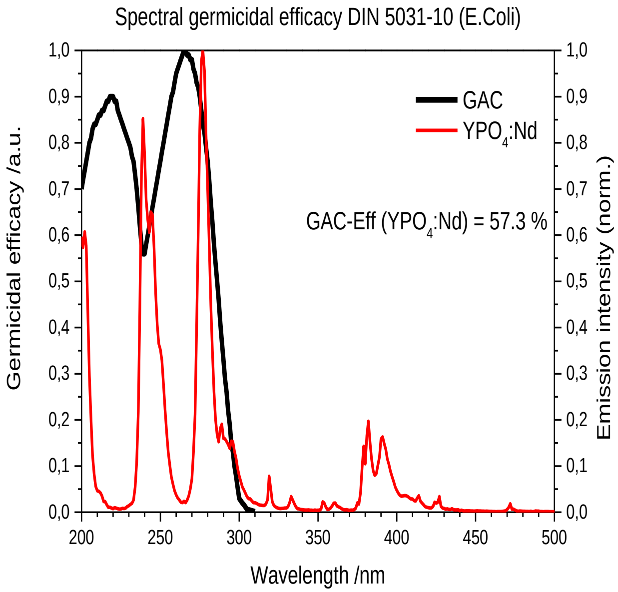
12. New Radiation Sources

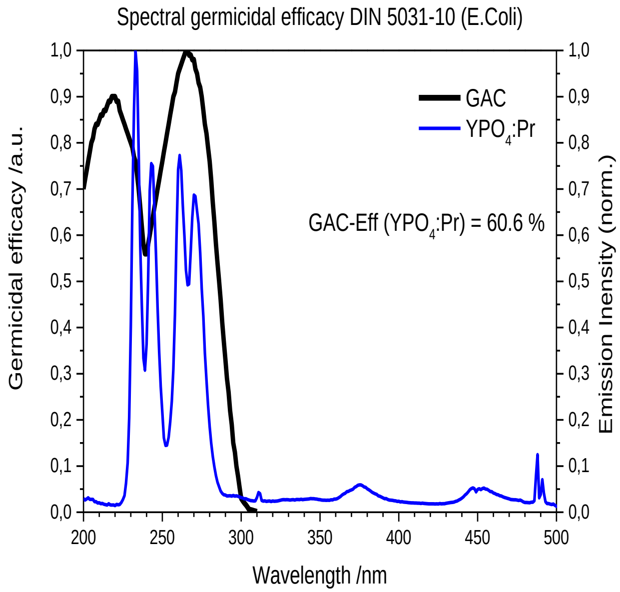
Converter for Xe Excimer Emitters: Radiation Resistant ortho-Phosphates

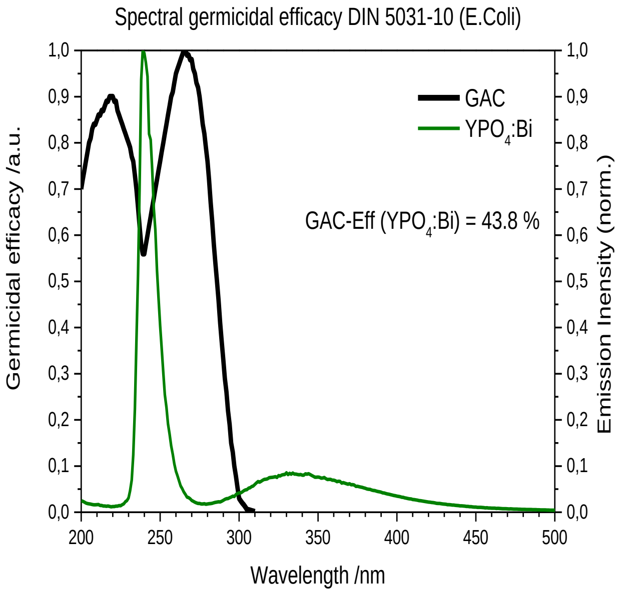
“Germicidal efficacy” (GAC)

$$E_{GAC}(Phosphor) = \frac{\int (Em_{Phosphor} \times GAC)}{\int Em_{Phosphor}}$$

GAC: Effectiveness of the inactivation of E. coli according to DIN 5031-10





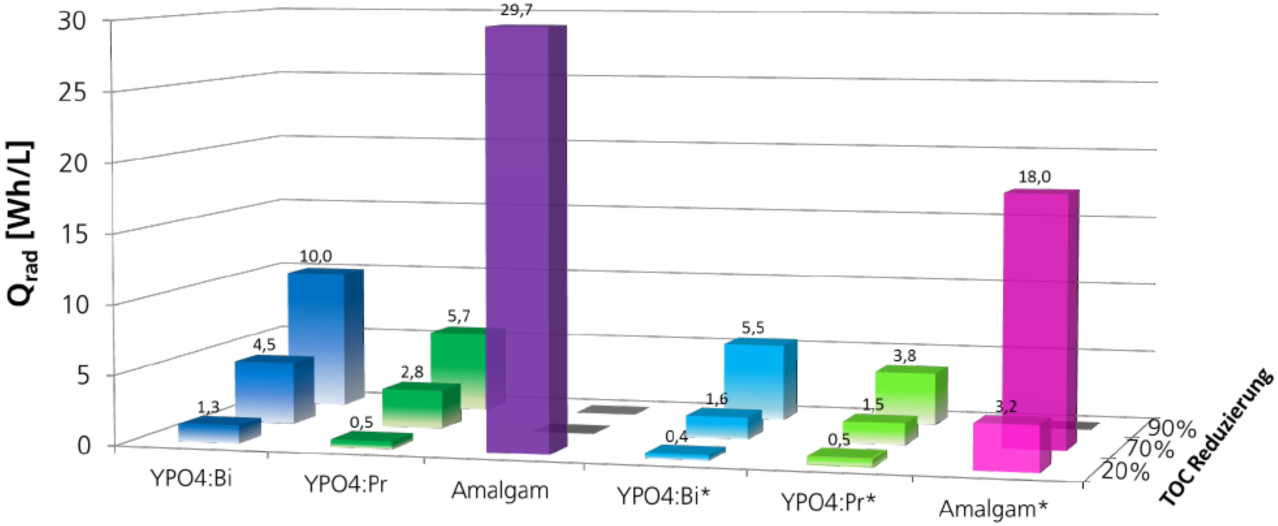


12. New Radiation Sources

Xe Excimer Lamps with Various UV-C Converter Materials

Source: N. Braun, GVB

Degradation of sulfamethoxazole (an antibiotic)



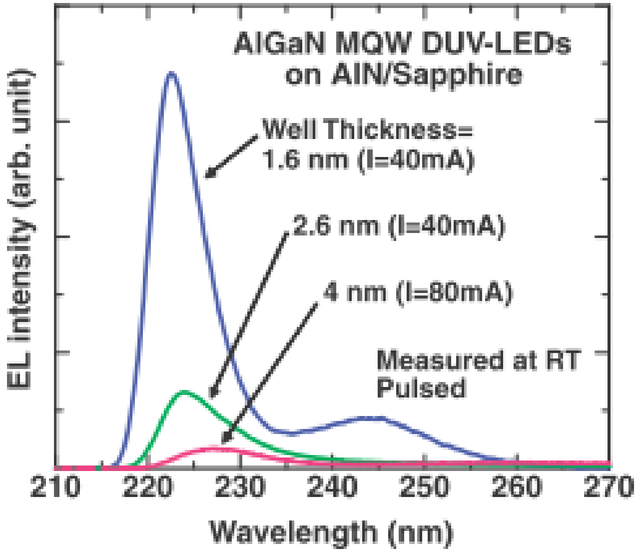
Source: Anke Nietzsch, DLR

Photolytic degradation via Xe excimer discharge lamps with a 225 or 235 nm converter allow energy savings of up to 95% compared to amalgam emitters

12. New Radiation Sources

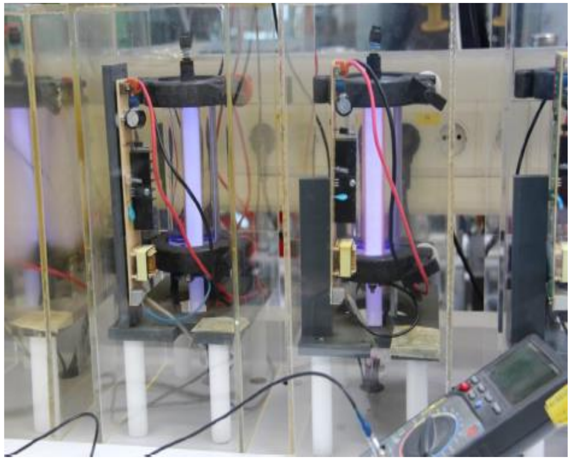
UV-Emitting LED / Laser Diodes

- Spectral range: Theoretical limit: 205 nm, experimental limit ~ 220 nm
- Heat dissipation determines yield & service life
- DUV-LED → DUV laser diodes: Sophisticated!
- Problems: spectral consistency, efficiency, light extraction, mass production, encapsulation, service life



UV-Emitting Xe-Excimer Lamps

- Spectral range : 172 – 400 nm
- Discharge and VUV converter determine yield & service life
- Hg-free, fast switching, high form factor
- Problems still to be solved: Efficient ECG, service life of converters, price, market access

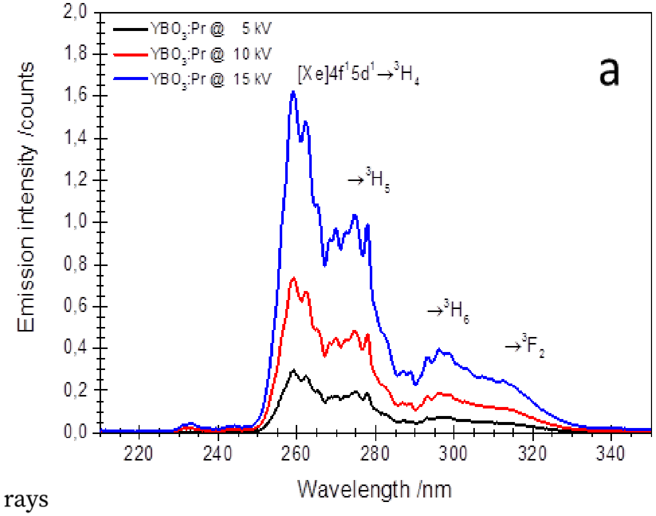


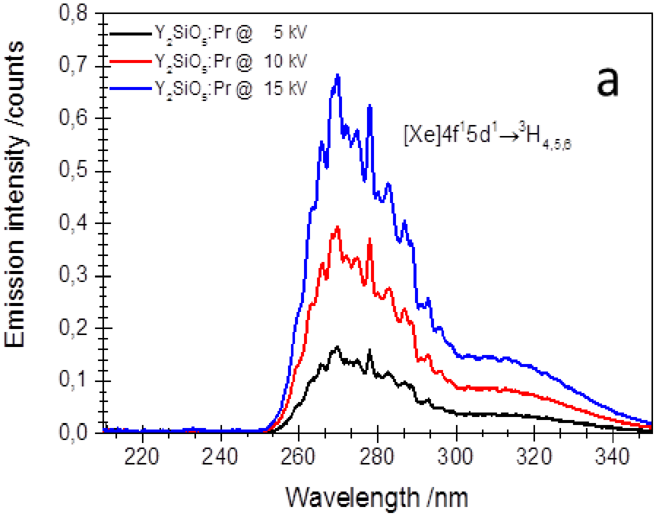
Source: N. Braun, GVB

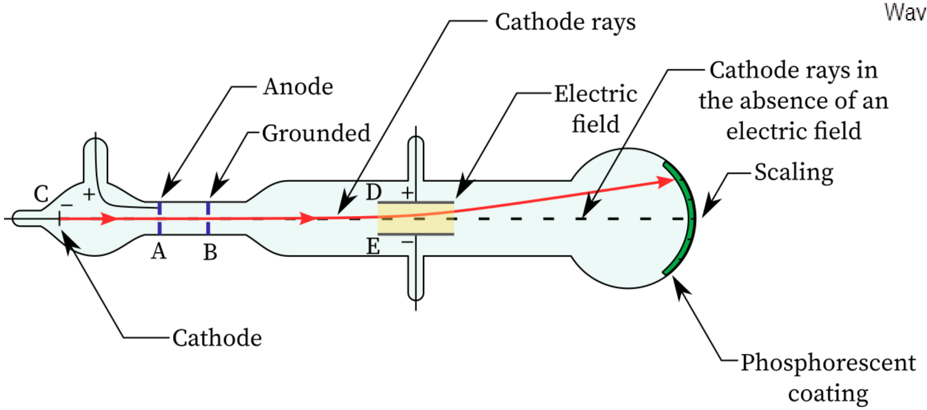
12. New Radiation Sources

Cathode-Ray-Tube (CRT) with UV-C Converter YBO_3:Pr or Y_2SiO_5:Pr

Miniature CRT as well as YBO_3:Pr and Y_2SiO_5:Pr^{3+} Emission spectra under e^- excitation







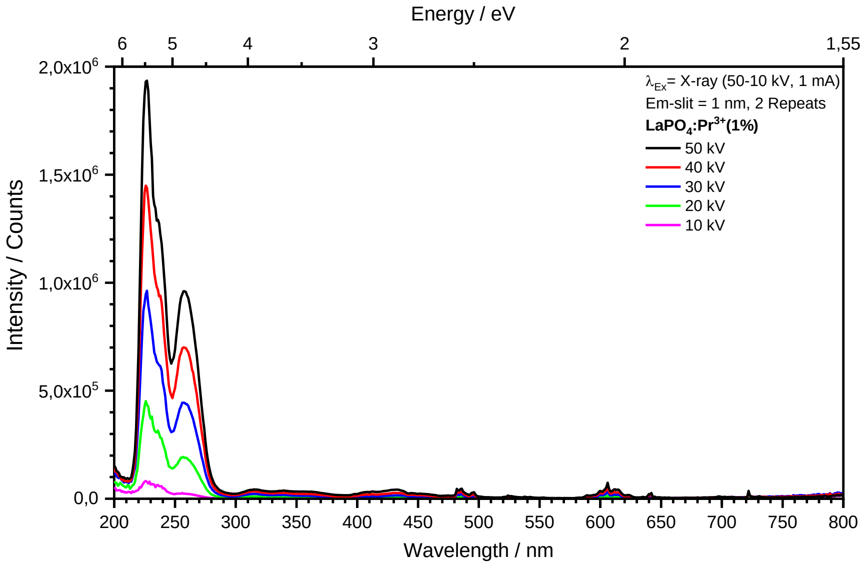
Accelerated electrons hit a phosphor screen to yield cathodoluminescence (CL): The principle is similar to that of a Braun tube for TV sets/monitors

Lit.: J. Silver, M. Broxtermann, T. Jüstel et al., ECS J. SSST 6 (2017) R47

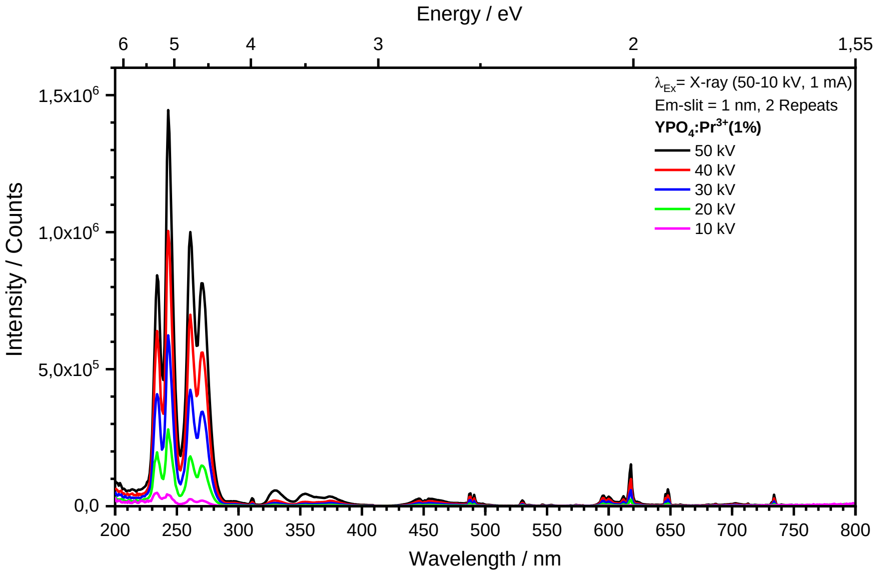
12. New Radiation Sources

X-ray Tube with UV-C Converter $LaPO_4$:Pr or YPO_4:Pr

$LaPO_4$:Pr upon 10 – 50 keV excitation



YPO_4:Pr upon 10 – 50 keV excitation



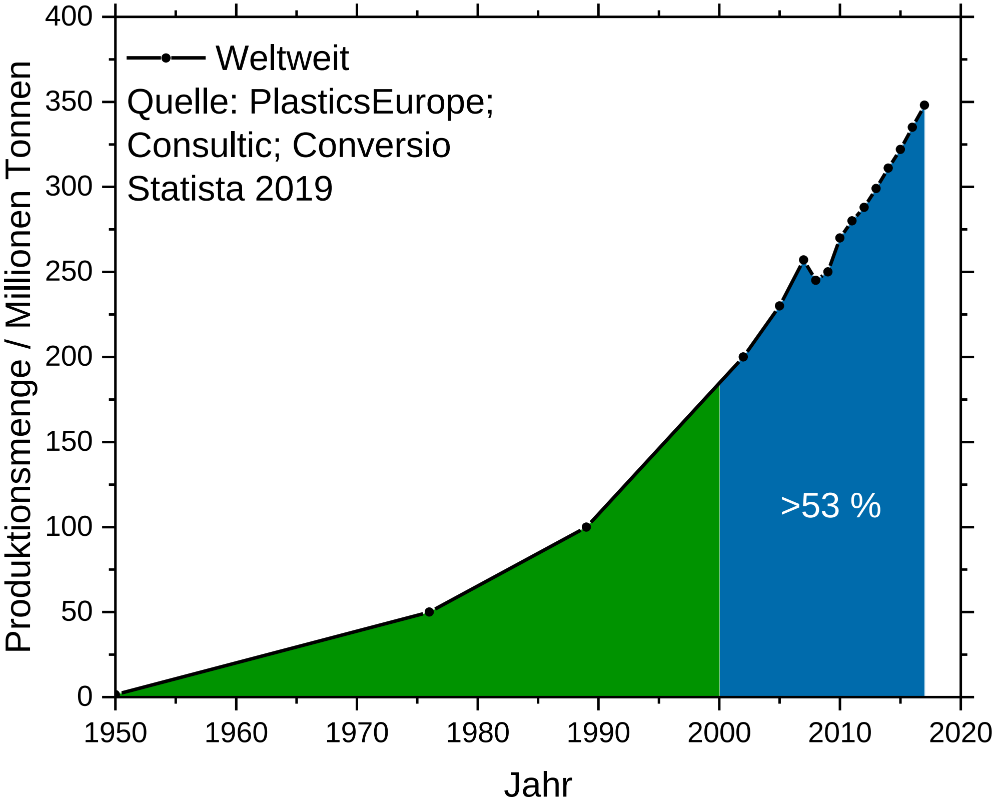
Pr^{3+} doped ortho-phosphates ($LuPO_4$) and ortho-silicates (Lu_2SiO_5) are efficient UV-C emitting scintillators

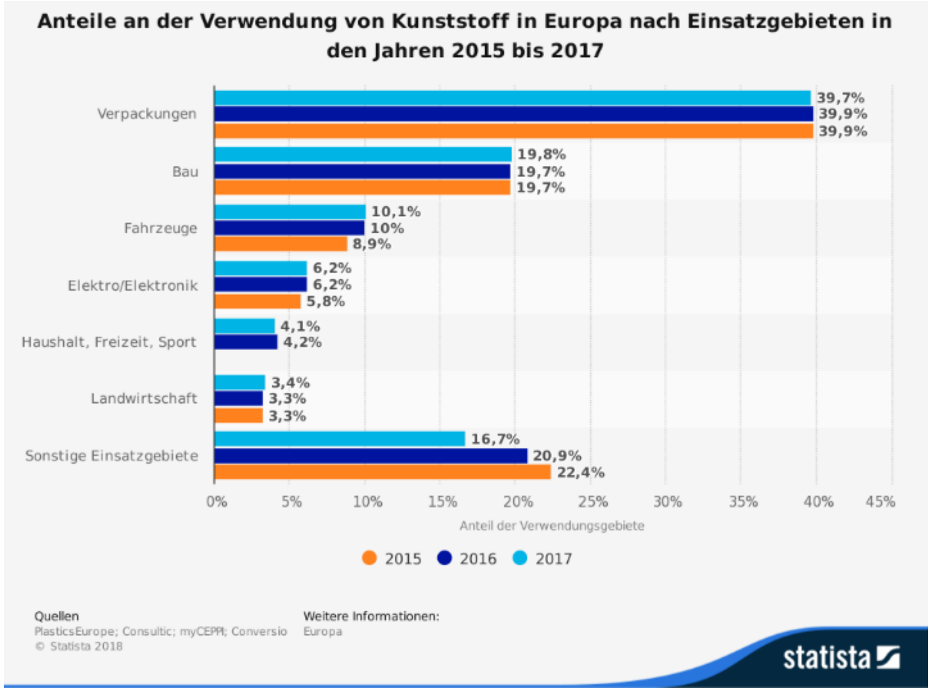
Many spin-offs, e.g. cancer & inflammation treatment by $LnPO_4$:Pr,Nd (Ln = Y, La, Lu)

Source: Jan Kappelhoff

13. Microplastic Degradation

Suspended Solids: Development of Plastics Production




Anteile an der Verwendung von Kunststoff in Europa nach Einsatzgebieten in den Jahren 2015 bis 2017

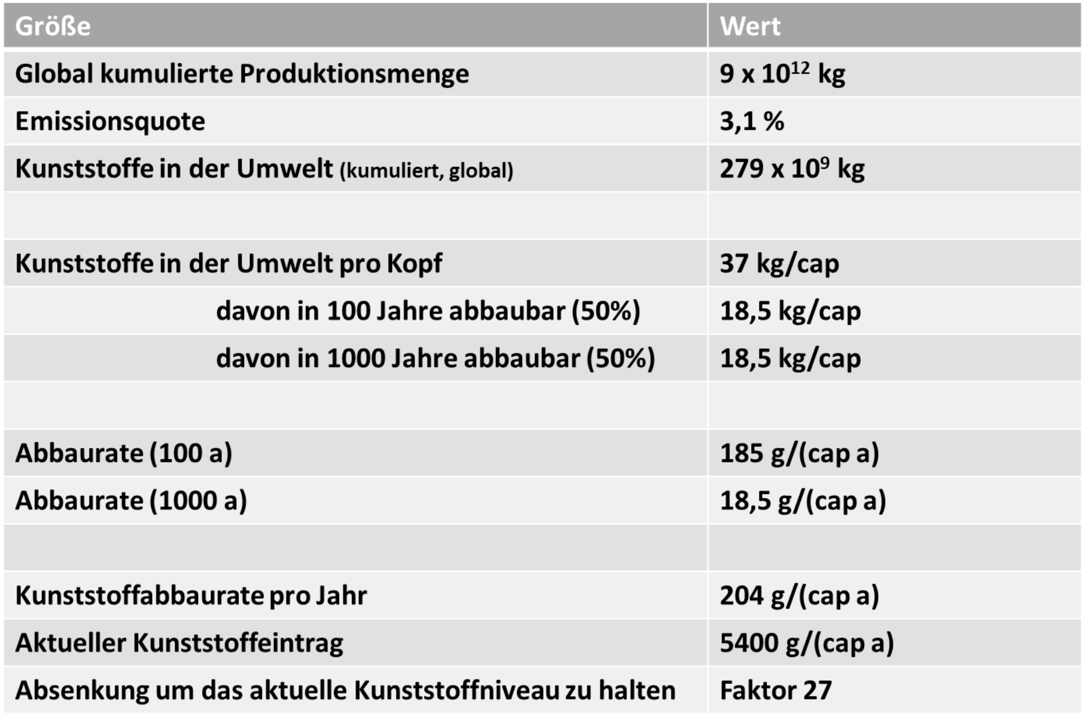
Quellen
PlasticsEurope; Consultic; myCEPPI; Conversio
© Statista 2018

Weitere Informationen:
Europa

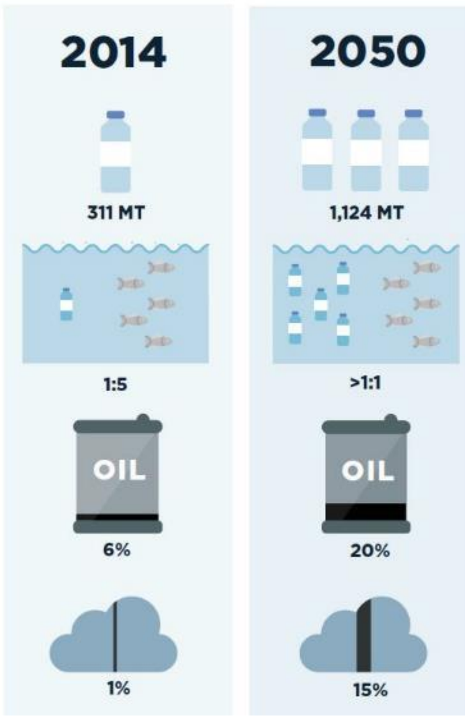
Around 8.3 billion tons of plastic have been produced to date (2017)

13. Microplastic Degradation

Suspended Solids: Plastic Input and Degradation in the Environment



Größe	Wert
Global kumulierte Produktionsmenge	9 x 10^{12} kg
Emissionsquote	3,1 %
Kunststoffe in der Umwelt (kumuliert, global)	279 x 10^{9} kg
Kunststoffe in der Umwelt pro Kopf	37 kg/cap
davon in 100 Jahre abbaubar (50%)	18,5 kg/cap
davon in 1000 Jahre abbaubar (50%)	18,5 kg/cap
Abbaurate (100 a)	185 g/(cap a)
Abbaurate (1000 a)	18,5 g/(cap a)
Kunststoffabbaurate pro Jahr	204 g/(cap a)
Aktueller Kunststoffeintrag	5400 g/(cap a)
Absenkung um das aktuelle Kunststoffniveau zu halten	Faktor 27



Plastics production

Plastic: fish ratio(in weight)

Global oil consumption for plastics production

Share of CO_2-emissions

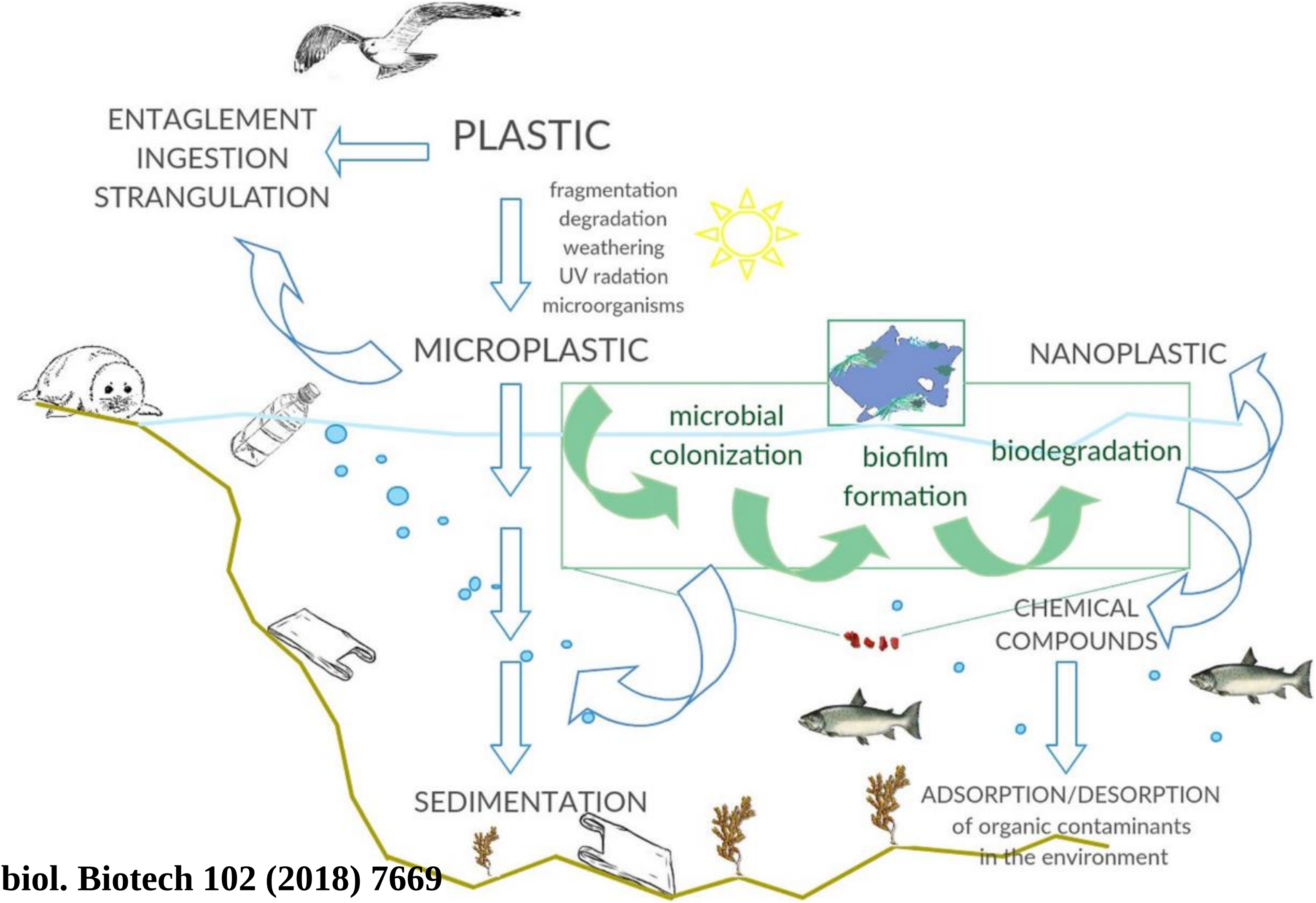
Source: Fraunhofer UMSICHT, Oberhausen

Source: Ellen MacArthur Foundation

We need to reduce the amount of plastic waste entering the sea by a factor of 27 in order to stabilize the current plastic content!

13. Microplastic Degradation

Suspended Solids: Microplastic Formation and Degradation



PLASTIC

ENTAGLEMENT
INGESTION
STRANGULATION

fragmentation
degradation
weathering
UV radation
microorganisms

MICROPLASTIC

NANOPLASTIC

microbial
colonization

biofilm
formation

biodegradation

CHEMICAL
COMPOUNDS

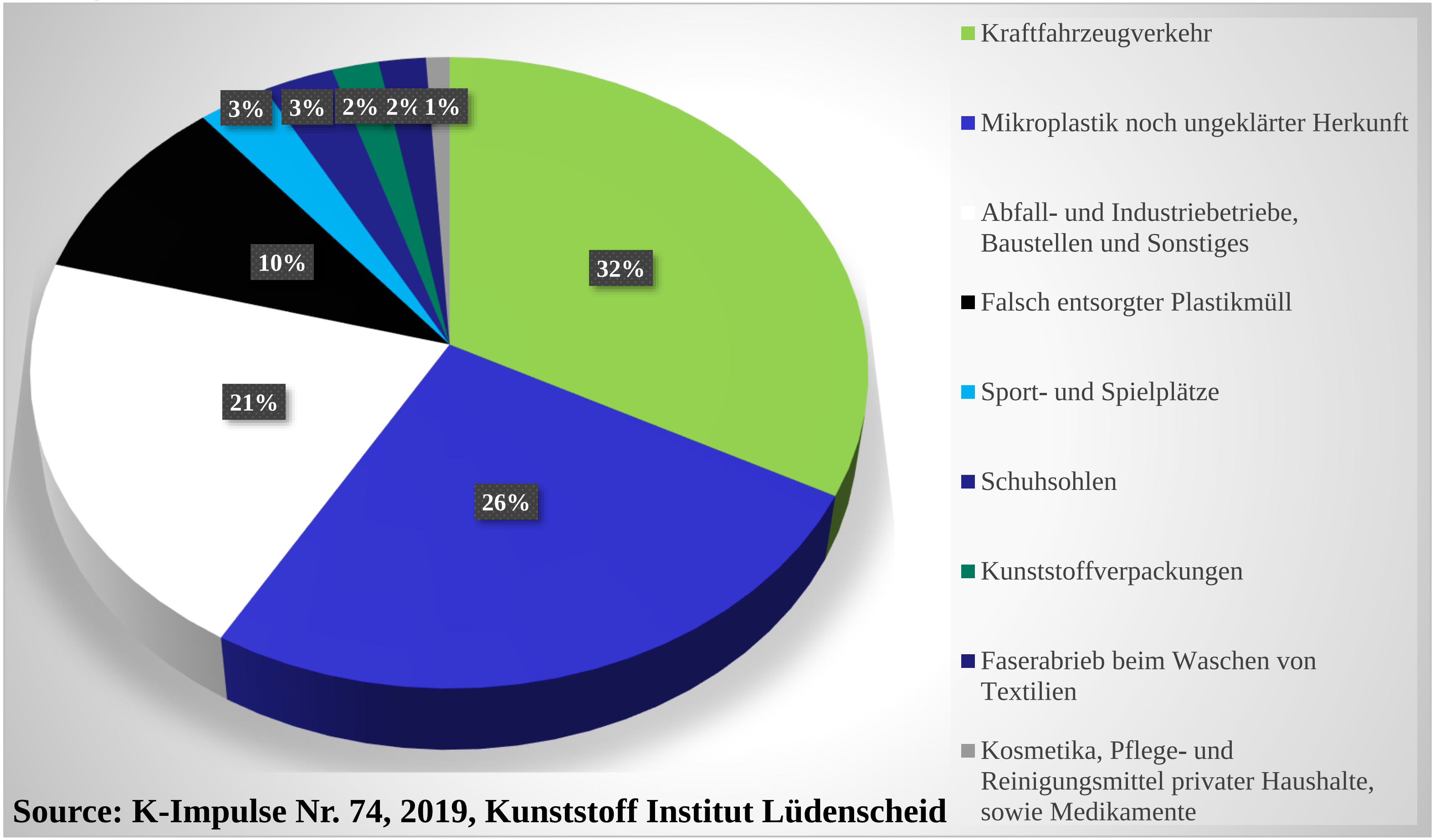
SEDIMENTATION

ADSORPTION/DESORPTION
of organic contaminants
in the environment

Source: Appl. Microbiol. Biotech 102 (2018) 7669

13. Microplastic Degradation

Origin of the Microplastics



Source: K-Impulse Nr. 74, 2019, Kunststoff Institut Lüdenscheid

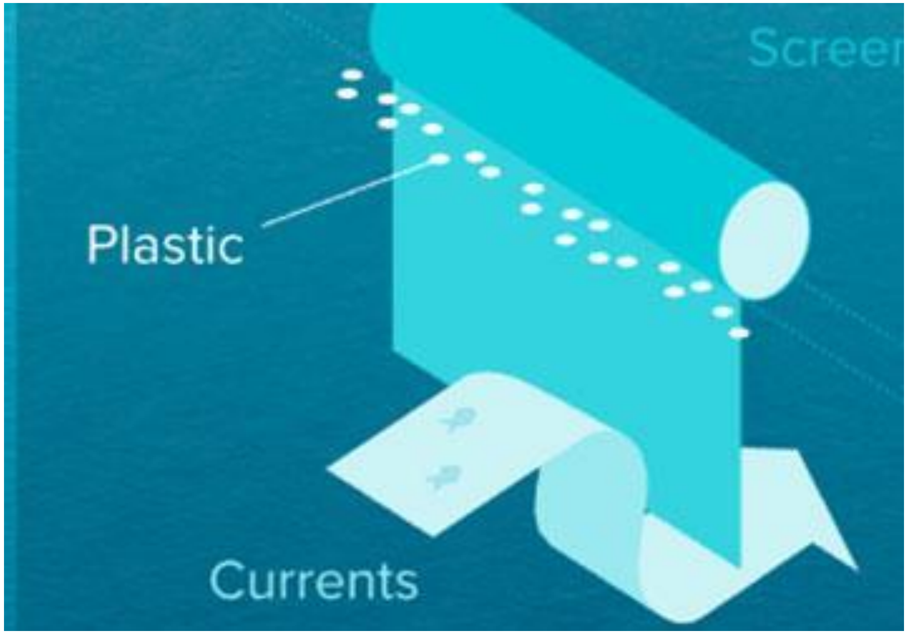
<u>Germany</u>
330,000 tons of microplastic end up per year into the environment

Cosmetics (1% share) use 500 tons of microplastics per year (Germany)

A good quarter of microplastic emissions come from unknown sources

13. Microplastic Degradation

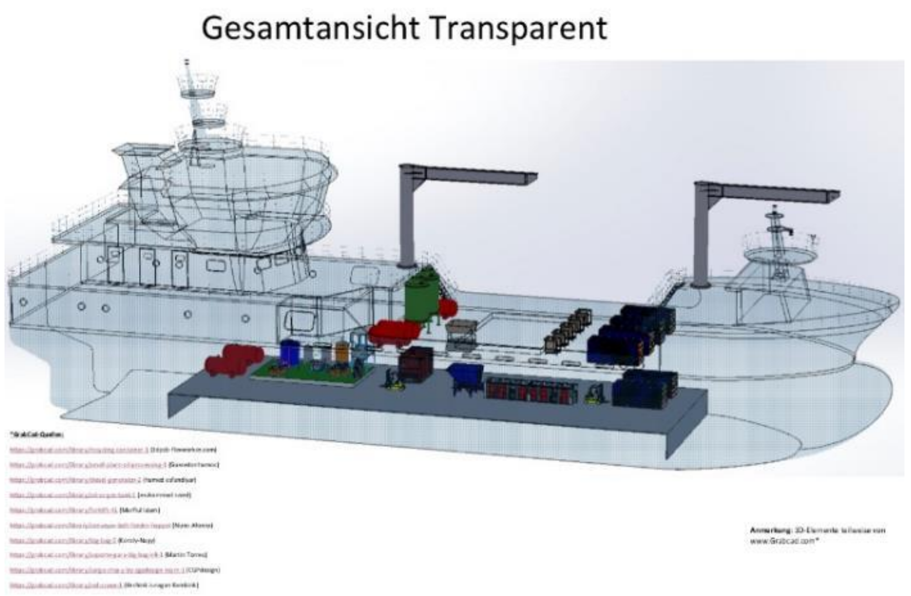
Project „The Ocean Clean Up“

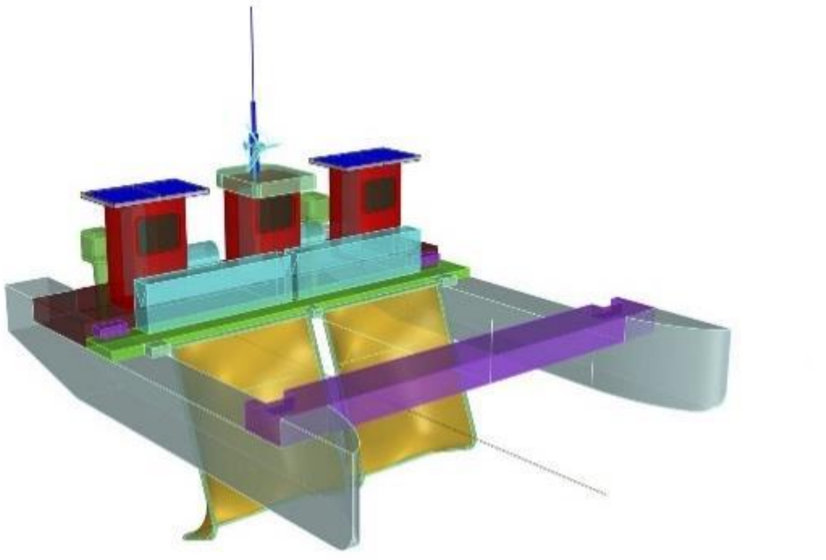


- The plastic is captured via barriers
- A ship regularly comes and collects the plastic
- The plastic is recycled
- Budget: Around 30 million Euros

13. Microplastic Degradation

Project „One Earth one Ocean“





- **Waste collection ships travel across the plastic carpet**
- **Both for estuaries and coastal areas**
- **The waste is taken to a central recycling ship and recycled**
- **ZIM-Project (BMWi)**
- **Problem: Sea surface ~ 361 Mio. km^2 (70.8% of the earth's surface)**

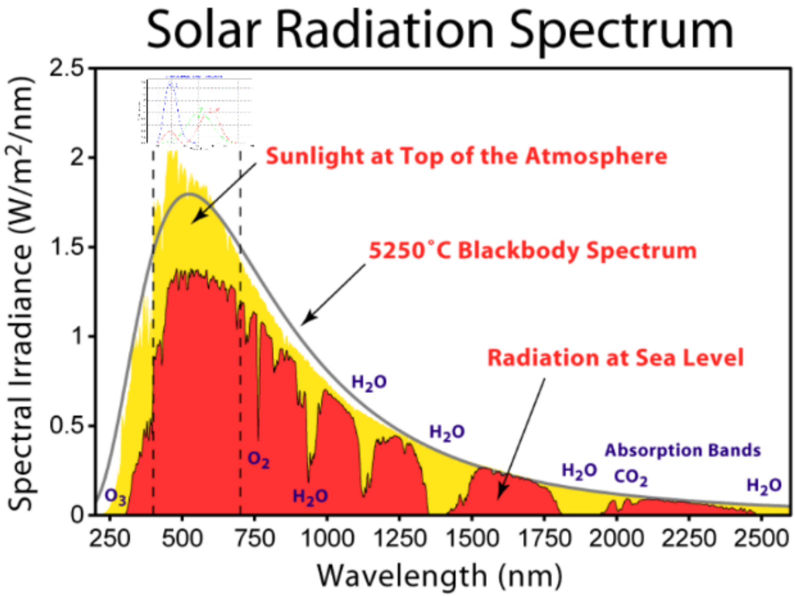
13. Microplastic Degradation

Photochemical Degradation of Microplastics

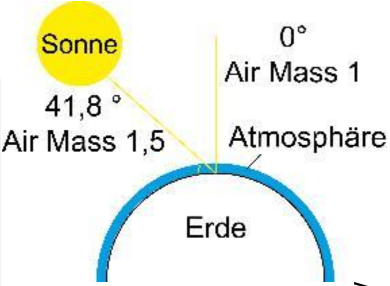
Solar constant E_e = 1.37 kW/m², Spectral components at mid-latitude

300 – 400 nm	400 – 500 nm	500 – 600 nm	600 – 700 nm	>700 nm
5,3%	18,2%	20,2%	18,7%	37,6%

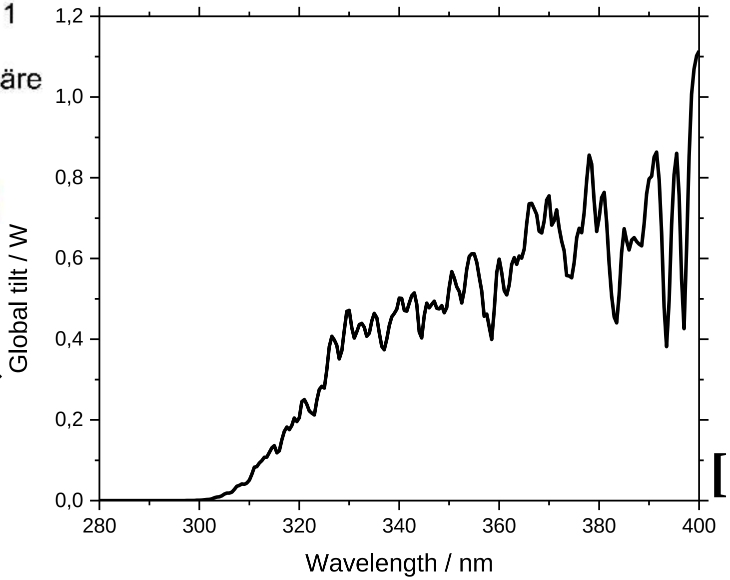
UV irradiance
~ 50 W/m²



[1]



Magnification of UV range



[2]

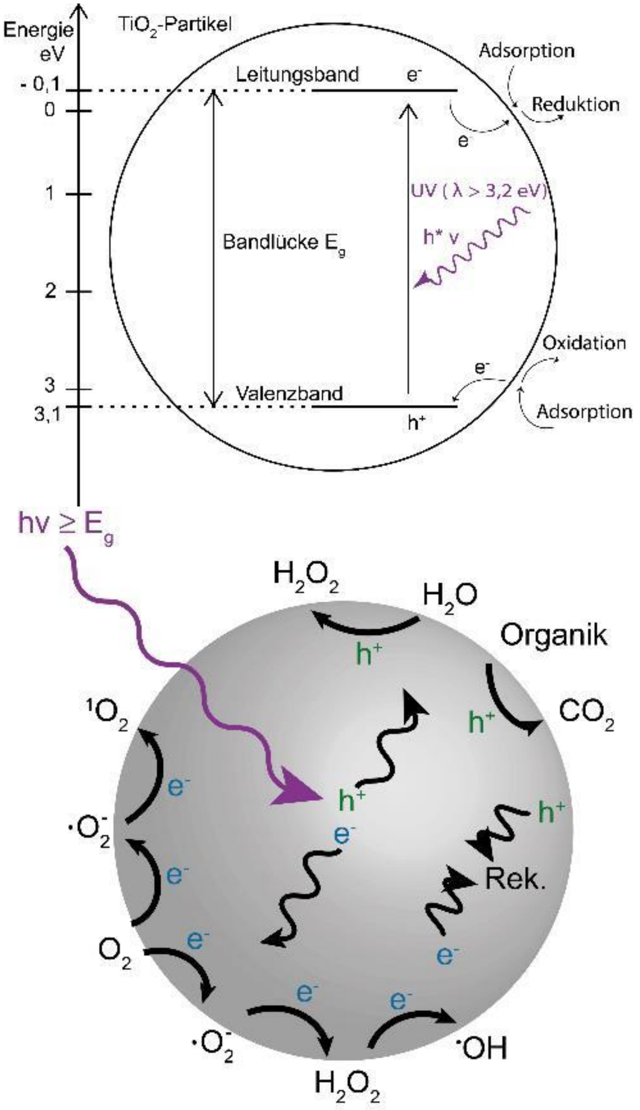
Sources: [1] https://kevinbinz.files.wordpress.com/2014/09/tunneling-solar-radiation-with-tunneling.png
[2] http://rredc.nrel.gov/solar/spectra/am1.5/

13. Microplastic Degradation

Photocatalytic Degradation of Microplastics byTiO$_2$

- **High refractive index (n_D > 2.5)**
- **High light scattering capacity**
- **Areas of application as a white pigment inpaints, varnishes, printed matter, plastics, cosmetics, foodstuffs, pharmaceuticals, toothpasteFood additive (E 171)**
- **Three modifications: Rutile, anatase & brookite**
  - **Rutile: Used as a white pigment, typically in plastics ~ 1% Rutile**
  - **Anatase: Use as a nanoscale catalyst →**

$$C_xH_{y/2} + (x + 1/4\ y)\ O_2 \rightarrow x\ CO_2 + y\ H_2O$$

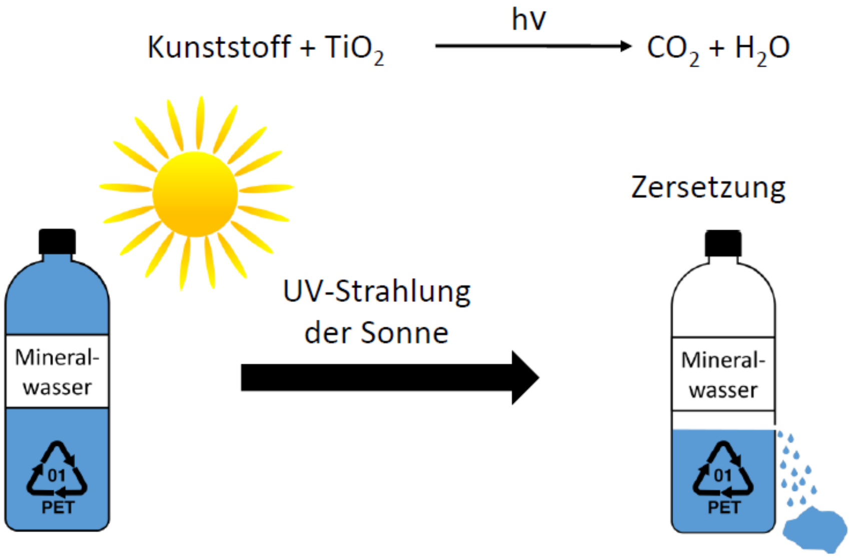


13. Microplastic Degradation

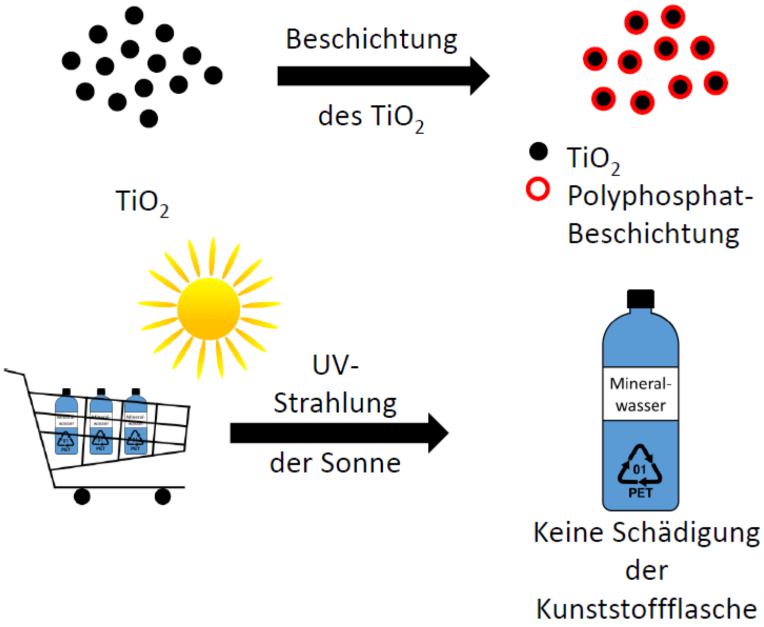
New Approach to Breakdown Microplastics by TiO_2

Idea: Incorporation of a catalyst inactivated by coating into the plastic, whereby the properties of the plastic should not change

a) TiO_2 breaks down plastics/microplastics



b) Inactivation through particle coating
Stability of the coating in fresh water



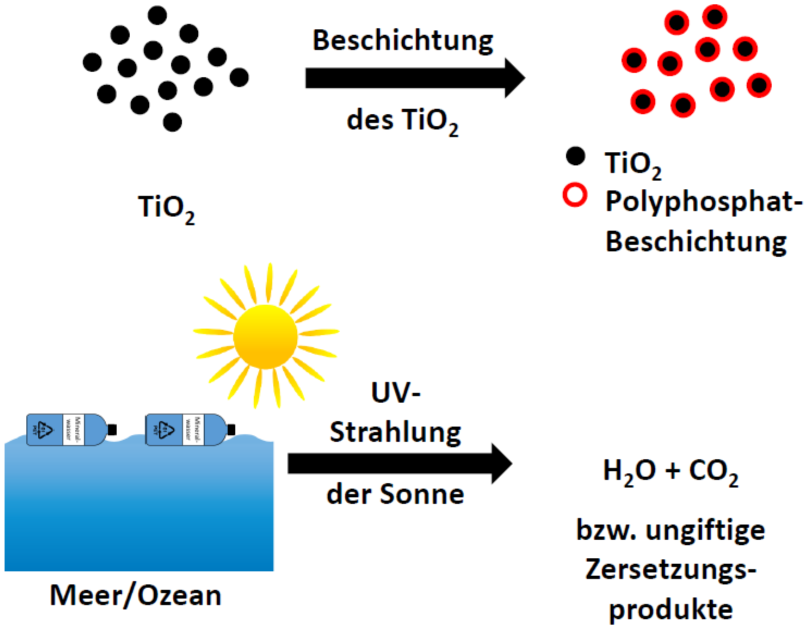
Lit.: M. Volhard, J.J. Christ, M. Blank, T. Jüstel, Sustainable Chemistry and Pharmacy 16 (2020) 100251

13. Microplastic Degradation

New Approach to Breakdown Microplastics by TiO_2

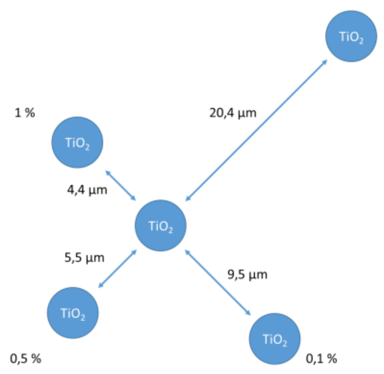
Idea: Incorporation of a catalyst inactivated by coating into the plastic, whereby the properties of the plastic should not change

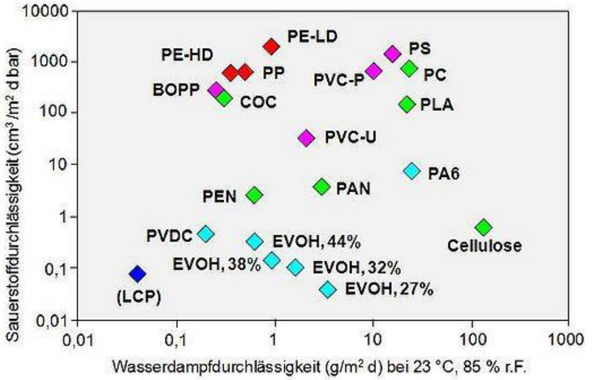
c) Activation in salt water by
Dissolution of the particle coating



Remaining problems

- **a) Distribution of nanoparticles in the polymer**
- **b) Diffusion barrier of the polymers**

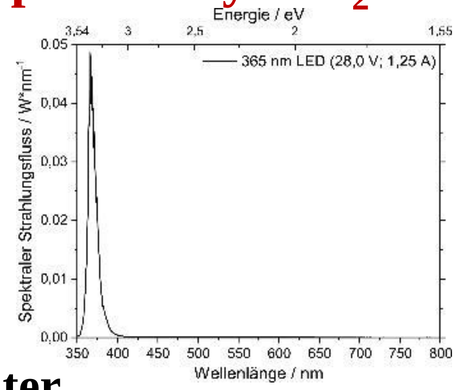


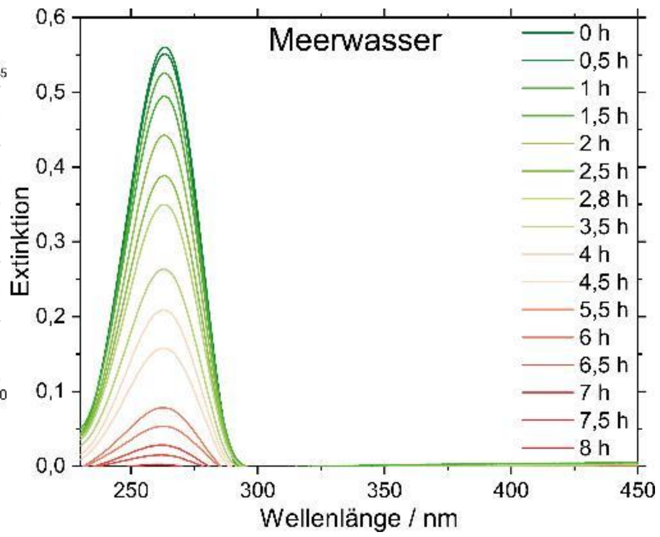


Source: https://wiki.polymerservice-merseburg.de/index.php/Barriere-Kunststoffe

13. Microplastic Degradation

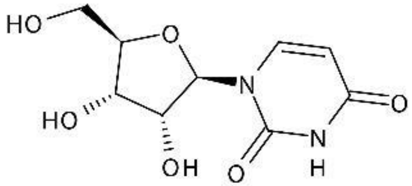
New Approach to Breakdown Microplastics by TiO_2



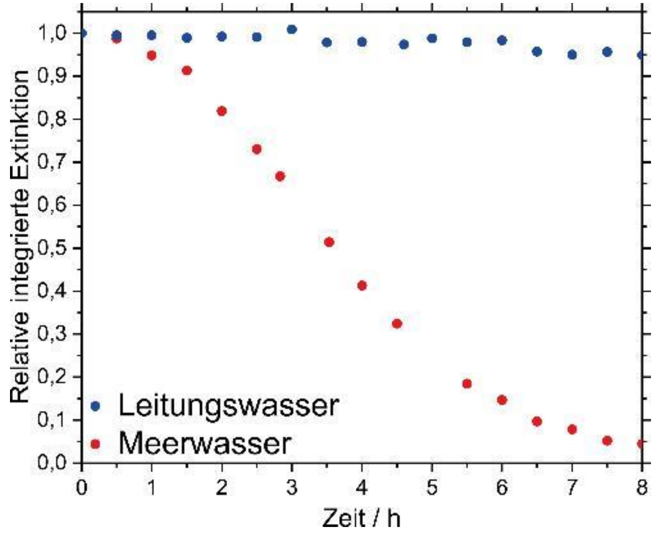


Result of the analysis of uridine with Ca-PP coated TiO_2(anatase) in tap water vs. seawater with irradiation with 365 nm, ~ 50 W/m^2:

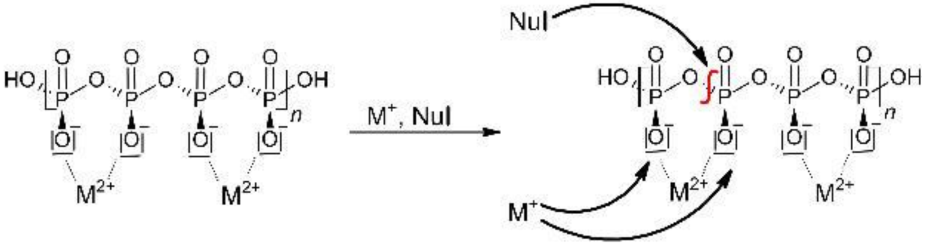
1. **Uridine is not decomposed in tap water**



Uridine (a UV-C actinometer)



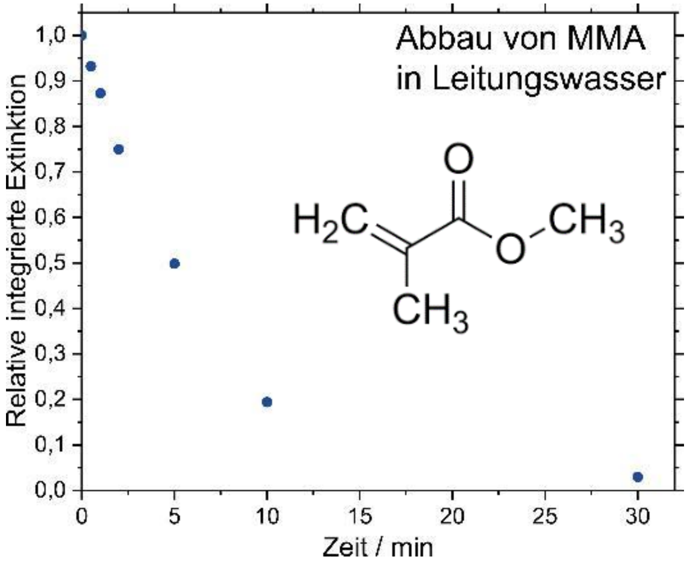
2. **Uridine is decomposed in seawater after 8 h**
   a) Ca-PP wird durch OH$^-$ und Mg^{2+} zu P$_i$ abgebaut
   b) TiO_2 is activated: Uridine → $CO_2 + H_2O + NH_4^+$



13. Microplastic Degradation

New Approach to Breakdown Microplastics by TiO_2

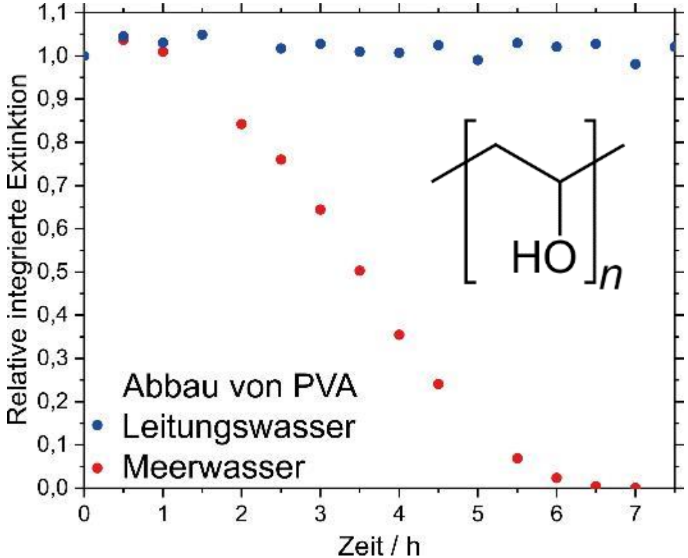
The monomer methacrylic acid methyl ester (MMA) is soluble in water. It can be completely decomposed by the photocatalyst TiO_2 (anatase) when irradiated with a 365 nm LED in tap water



Polyvinyl alcohol (PVA) is a water-soluble polymer

With the help of H_3BO_3 and I_2/KI the polymer can be colored and detected photometrically

In contrast to seawater, no decomposition could be detected in tap water by 365 nm irradiation in the presence of Ca-PP coated TiO_2(anatase).



14. Outlook

Alternative Use of the Radiation Sources

- **Air disinfection and purification, e.g. to combat (corona) viruses**

https://www.ledsmagazine.com/lighting-health-wellbeing/article/14177977/boston-university-validates-signify-uvc-for-coronavirus-deactivation

https://www.laborpraxis.vogel.de/uv-c-strahlung-schaltet-coronaviren-das-licht-aus-a-981217/?cmp=nl-102&uuid=105DF3D6-2FE8-4992-9BFA289668FAE305

- **Increasing demands on process water disinfection and purification**

https://www.ledsmagazine.com/lighting-health-wellbeing/article/14177977/boston-university-validates-signify-uvc-for-coronavirus-deactivation

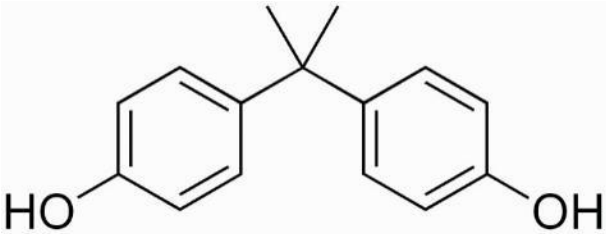
https://www.laborpraxis.vogel.de/uv-c-strahlung-schaltet-coronaviren-das-licht-aus-a-981217/?cmp=nl-102&uuid=105DF3D6-2FE8-4992-9BFA289668FAE305

New Problem Areas in the Water Sector

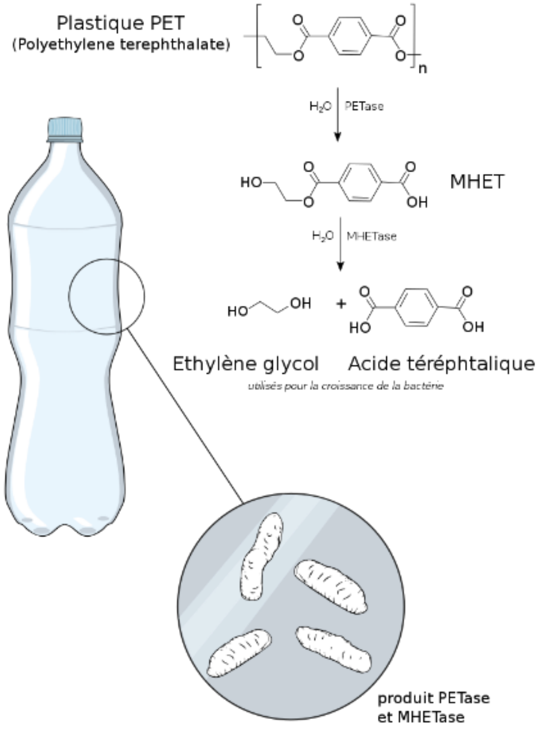
- **Increasing number of micropollutants and new substances (e.g. PFAS)**
- **Increase in water temperature in the supply networks (climate change)**
- **Increasing nitrate input**
- **Steadily increasing concentration of micro- and nanoplastics**
- **„New“ heavy metal exposures : Ga, In, Co, Nb, Ta, U, …..**

14. Outlook

Degradation of Plastic Additives and Microplastics



- **Photodegradation of common plastic additives such as diethylhexyl phthalate or bisphenol A**
- **Combined use of photocatalysts with enzymes in drinking water treatment**
  a) TiO_2 Anatase leads to fragmented and porous plastic particles
  b) PETase depolymerises the polymer
  c) MHETase degrades the ester to glycol and terephthalic acid
  d) TiO_2 Anatase mineralises terephthalic acid (glycol is degraded microbiologically)



Lit.: Nature Communications 10 (2019) 1717, „Structure of the plastic-degrading Ideonella sakaiensis MHETase bound to a substrate"

14. Outlook

Useful Internet Addresses

- **Drought monitor of the Helmholtz Centre: https://www.ufz.de/index.php?de=37937**
- **Ruhr Dam Control Centre: https://www.talsperrenleitzentrale-ruhr.de/**
- **Internet of Water: https://internetofwater.org/**
- **Care 222 Technology : https://www.ushio.eu/de/care222-uv-desinfektion-2/**
- **Struvite/fertiliser from sewage treatment plant effluent: https://www.deutschlandfunk.de/struvit-duengemittel-aus-klaeranlagen-abwaessern-100.html**
- **Xe-Excimer (Instant Trust Marine): https://www.instanttrust.nl/en/**
- **UV light-emitting diodes from the Ferdinand Braun Institute : https://www.fbh-berlin.de/forschung/photonik/chips-laser-leds/uv-leds**

14. Outlook

Further Internet Addresses

Enviolet	**https://www.enviolet.com/**
Heraeus	**https://www.heraeus.com/de/group/home/home.html**
Homepage T. Jüstel	**https://www.fh-muenster.de/juestel**
LG Innotek	**https://www.lginnotek.com/main/main.do**
Lightlab	**https://www.lightlab.com/**
Nichia	**https://www.nichia.com/**
Peschl Ultraviolett	**https://peschl-ultraviolet.com/**
Philips / Signify	**https://www.signify.com/de-de**
Radium	**https://www.radium.de/de**
Robert-Koch-Institute	**https://www.rki.de**
Stanley Electric	**https://www.stanley.co.jp**
TECE	**https://www.tece.com/de**
Ushio	**https://www.ushio.com**
UV-Technology	**https://www.uvtechnik.com/**
Xylem	**https://www.xylem.com/de-de/**