1.2 The physicochemical properties of water and their relevance for life

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SUMMARY: *As component of both organic and inorganic substances as well as in its function as solvent, reaction and transport medium, water is essential for all abiotic and biotic processes on Earth. Due to its ability of forming intermolecular hydrogen bonds, water possesses a range of particular physicochemical properties which are of fundamental relevance for the matter and energy budgets of ecosystems. This chapter gives an overview of the most important physicochemical properties of water and their relevance for life on Earth.*

What makes the Earth so comfortable? Without exaggerating, one can state that water plays a vital part, as there wouldn't be any life without water. *Table 1.2-1* provides some examples of the amount of water in several organisms.

Forms of water

Water – with its formula H_2O – is the only inorganic compound existing in its solid, liquid and gaseous physical state under natural conditions. Water serves as a medium for the transformation of highly complex organic molecules that form the basis for life processes. The reason for many of liquid water's special properties originates from the water molecules consisting of dipoles that associate through intermolecular hydrogen bonds in its condensed phase (*Fig 1.2-1*).

The phenomenon of hydrogen bonding

This type of bond is of fundamental significance for the development of life and life processes. The uniqueness of water compared to other – also hydrogen bonded – liquids is the existence of a three dimensional network. This causes particularly strong intermolecular interactions between water molecules in their condensed phase. Among all bond

Table 1.2-1: Mass fraction of water in various organisms and tissues.

Organism	Water content in %
Jellyfish	98
Snail	95
Man (70 kg)	60
Fat tissue	23
Bones	28
Muscles	70
Liver	71
Brain	75
Blood	84
Insects	>50
Desert plants	40 ... 2

types, Linus Pauling ascribes the greatest significance in physiology to the hydrogen bond.

A hydrogen bond can form if two atoms X and Y – in general very electronegative elements like fluorine, oxygen or nitrogen – are connected to a group X–H•••Y through a hydrogen atom. In this arrangement, the hydrogen atom is located asymmetrically and bound stronger by one of the atoms, e.g. X, instead of being situated half way between both other atoms (see *Fig 1.2-1*). The hydrogen atom, however, does penetrate the electron cloud of the atom Y to a certain degree. Typical bond energies of hydrogen bonds are 20 kJ/mol – about a quarter of the bond energy of

Bond angle	H-O-H	104.3°		
Interatomic distance		**Gas phase** *(isolated molecule)*	**Liquid**	**Ice Ih**
$d(O–H)_{INTRA}$	(a)	0.096 nm[1]	0.098 ... 0.100 nm D_2O [2,3] H_2O [3]	0.101 nm[1]
$d(O–O)_{INTER}$	(c)		0.285 [4]... 0.289[3] nm	0.276 nm[1]
$d(O–H)_{INTER}$	(b)		0.195[4] ... 0.200[3] nm	
$d(H–H)_{INTER}$	(d)		0.240 nm[3]	
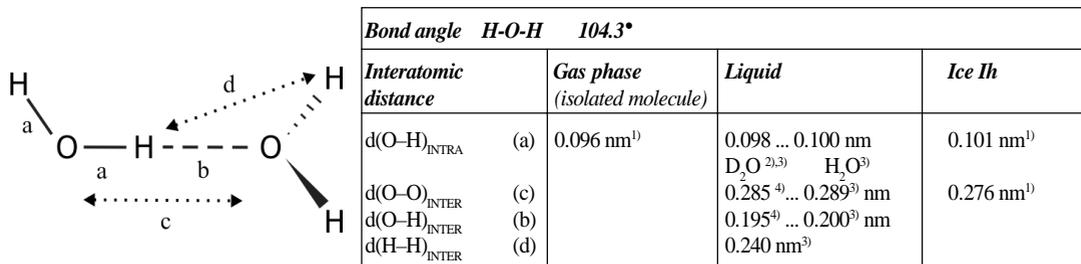
[1] ULLMANN (1996)   [2] POWLES (1981)
[3] GABALLA & NEILSON (1983)   [4] KÁLMÁN et al. (1977)

Fig. 1.2-1: Geometry of the water molecule and energetically favoured configuration of two molecules in condensed phase.

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a covalent bond – and bond distances are between 0.25 and 0.3 nm.

In the case of hydrogen bonds in water, different experimental methods have yielded bond energies between 19 and 22 kJ/mol. As such, the almost linear O–H•••O arrangement of a water dimer, as it exists in ice (shown in *Fig 1.2-2*), is also energetically very favourable in the liquid phase.

Physicochemical characteristics

Various anomalies of water at temperature ranges of up to 100 °C are a result of hydrogen bonding. Some important properties are listed in *Table 1.2-2*.

When comparing these properties to those of atomic or non-hydrogen bonded molecular liquids of similar molecular size some particularities are noteworthy:

• The melting point of ice is exceptionally high if compared to the decrease in melting points with decreasing atomic number among the hydrides of the sixth main group. Water shares this behaviour with various hydrides and halogenides of the 4th, 5th, 6th, and 7th group. Among these groups, the first elements show extremely high melting and boiling points.

• During the melting of ice at atmospheric pressure, the volume contracts by 8.2%. This anomalous contraction of volume – most substances expand during melting – leads to a decrease in freezing point with increasing pressure: »ice melts under pressure«. At 0 °C the freezing point is decreased by 1 °C with a pressure of 1.33×10^7 Pa.

• The dependence of liquid water's molar volume on pressure and temperature exhibits extremes. The density of liquid water has a maximum at 3.98 °C.
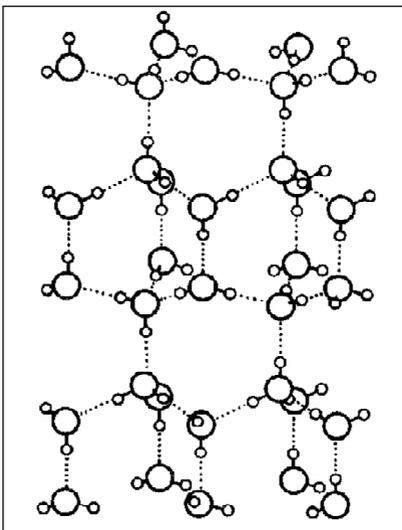

Fig. 1.2-2: Structure of the solid phase (ice: modification Ih).

• The thermal expansion coefficient α of liquid water is one order of magnitude smaller compared to other molecular liquids. The isothermal compressibility χ_T shows that for a molecular liquid water is rather incompressible.

• The dynamic viscosity of water is higher than that of comparable, non-hydrogen bonded liquids. Furthermore, the pressure dependence of the viscosity is anomalous: the viscosity decreases with pressure and reaches a minimum at about 60 MPa (this pressure is equivalent to a water column of 6 km).

• Water's surface tension is higher than that of other liquids, including most other hydrogen bonded liquids.

• Within a temperature range of up to 130 °C, liquid water's thermal conductivity increases with increasing temperature.

• Liquid water possesses a high specific heat capacity at constant pressure, which changes only slightly up to 100 °C.

• The enthalpy evaporation $\Delta_{vap}h$ of water is anomalously high. Similar to the specific heat capacity, $\Delta_{vap}h$ is almost four times as high as those for other comparable, non-hydrogen bonded liquids. This difference is ascribed to the hydrogen bond. In addition, the enthalpy of evaporation of water is very high compared to its enthalpy of melting.

The fact that water expands while freezing has led, amongst other consequences, to our familiar picture of nature, e.g.: Water easily penetrates rock crevices. When it freezes, the rock is further disrupted, physical and chemical weathering occurs, and, ultimately, soil is formed.

The fact that water exhibits its highest density at 4 °C, but not at its freezing point (*Fig 1.2-3*), is essential for the thermal stratification and the circulation of lakes. This leads to the freezing of water bodies from their surface towards the ground. Not only is this of importance for aquatic life of inland waters, but it is also crucial for the oceans. If the colder regions of the oceans were to freeze from the bottom to the top, energy received by the sun's radiation during summer would only be sufficient to thaw the uppermost layers. Thus, the cycling of energy and matter which relies on the circulation of the oceans would cease partially or even completely.

The enormous specific heat capacity of water is responsible for its ability to store vast amounts of energy. In this way, water currents, as for example the Gulf Stream, carry gigantic amounts of heat from warmer climate zones into colder ones. Thus, the oceans work as huge thermostats. Not only the Earth's climate, but also the heat regulation of organisms depends on the high heat capacity of water. It contributes, for example, to the maintenance of a constant body temperature in warm-blooded organisms.

Property	Value
Molar mass M	18.012 g/mol
Standard enthalpy of formation $\Delta_f H^0$	-286.2 kJ/mol
Standard entropy of formation $\Delta_f S^0$	69.98 J/(mol×K)
Melting point θ_m	0°C
Boiling point θ_b	100 °C
Triple point	$\theta_t = 0.01$ °C, $p_t = 6.133 \times 10^2$ Pa
Critical point	$\theta_c = 373.98$ °C, $p_c = 22.05 \times 10^6$ Pa $\rho_c = 322$ kg/m^3
Density ρ liquid water Ice I	997.05 kg/m^3 (25 °C) 999.87 kg/m^3 (0 °C) 916.8 kg/m^3 (0 °C)
Thermal expansion coefficient α	257.1×10^{-6}/K (25 °C)
Isothermal compressibility χ_T	4.525×10^{-4}/Pa (25 °C)
Specific heat capacity c_p liquid water Ice	4.180 kJ/(kg×K) (25 °C) 4.191 kJ/(kg×K) (10 °C) 4.228 kJ/(kg×K) (0 °C) 2.072 kJ/(kg×K) (0 °C)
Vapour pressure p	3176.2 Pa (25 °C) 1228 Pa (10 °C) 611 Pa (0 °C)
Latent heat of vaporisation $\Delta_{vap} h$	2243.7 kJ/kg (25 °C) 2256.6 kJ/kg (100 °C)
Latent heat of fusion $\Delta_{fus} h$	333.69 kJ/kg (0 °C)
Cryoscopic constant K_f	1.853 K×kg/mol
Ebullioscopic constant K_b	0.515 K×kg/mol
Surface tension σ	7.423×10^{-2} N/m (10 °C) 7.20×10^{-2} N/m (25 °C) 5.891×10^{-2} N/m (100 °C)
Dynamic viscosity η	0.8903×10^{-3} Pa×s (25 °C) 1.307×10^{-3} Pa×s (10 °C)
Refractive index n	1.3325 für $\lambda = 589$ nm (25 °C)
Dielectric constant ε	78.46 (25 °C) 87.81 (0 °C)
Sound velocity c_{sound} in distilled water in sea water	 1496.7 m/s 1531 m/s
Thermal conductivity λ liquid water ice	 0.602 W/(K×m) (20 °C) 0.565 W/(K×m) (0 °C) 2.25 W/(K×m) (0 °C)
Ion product K_W	1.008×10^{-14} (pK_w=14.00) (25 °C) 0.292×10^{-14} (pK_w=14.53) (10 °C) 0.184×10^{-14} (pK_w=14.73) (5 °C) 0.114×10^{-14} (pK_w=14.94) (0 °C)

Table 1.2-2: Properties of water. If not stated otherwise, data refer to ordinary water with natural isotopic composition and atmospheric pressure (1 atm = 101 325 Pa).

Additionally, the relatively high thermal conductivity of water prevents serious local temperature fluctuations.

Very pure water has an electric conductivity of 0.03 μS/cm. This is due to the autoprotolysis of water (see Eq. 4). The electric conductivity measured on real water bodies, however, is significantly higher (see *Table 1.2-3*), which is mainly due to dissolved ionic water ingredients. Water, being a strong dielectric – water's dielectric constant is one of the highest known for liquids – is an excellent solvent for salts and gases, which are capable of solvolysis with subsequent dissociation (e.g. CO_2).

Another feature of water which is important for the hydrological cycle is its enthalpy of evaporation. Closely linked to this is the fugacity of water, which determines the amount of water that is converted into the gas phase and can be transported to the atmosphere.

Questions on the formation of the global hydrological cycle are not easily answered. Prerequisites for a hydrosphere as a requirement for life are:
• The planet must have acquired sufficient water to form oceans.
• This water must have penetrated from the Earth's interior to the surface.
• It must not be lost to space.
• It must be mostly available in its liquid state.

On Earth, all these requirements are met. Its basics are derived from the initial state of matter and comprise size, orbit, rotation and chemical composition of the Earth.

The blue planet

Terrestrial water is estimated to be at least 3.8 billion years old as this is the geological age of the oldest sedimentary rocks. Solid data on the genesis of terrestrial water are scarce, but there are several plausible theories. It can be assumed that the formation of planets resulted from the condensation of gases and accretion of matter due to gravity. Due to the heat produced during the manifold collisions as well as the fugacity of water it is unlikely that water occurred in its free form right from the beginning. Carbonaceous and siliceous components, however, were found in meteorites, which

included bound water (up to 20%). Therefore, the hypothesis seems plausible that water was brought to the Earth in a bonded state. The high temperatures inside the Earth could have led to a »distillation« of water from water-containing minerals. Subsequently, it could have formed a preliminary atmosphere – together with other volatile compounds, such as carbon dioxide, carbon monoxide, nitrogen, ammonia, and methane. During the cooling of the Earth, which occurred 4.5 billion years ago, water condensed on the Earth's surface while the carbon oxides and nitrogen remained in the gas phase.

The formation of the so-called juvenile water from outgassing of water bound in the Earth's interior is estimated to be about 0.3 km³/year in the current geological era.

The total amount of water on the Earth's surface can be assumed to be relatively constant throughout the geological timescales. This is due to the natural »cooling trap« which exists at an altitude of approximately 15 km above the Earth's surface and which prevents a loss of water to space. Solar radiation, being rich in energy, can lead to a photodissociation of water in the outer layers of the atmosphere. The so-produced hydrogen is lost to space, while most of the oxygen stays in the atmosphere. As only little amounts of water are available in the upper atmosphere, the amount of photodissociated water vapour which can be formed and lost to space is also small (4.8×10^{-4} km³/year).

The loss of gases from the surface to space is determined mainly by two factors: the gravitational force which is deduced from the mass and radius of the Earth and the mass of the molecule or the atom itself. These relationships are very sensitive. For example, doubling the molecular mass increases the loss to space by several orders of magnitude. Consequently, the amount of helium which is lost to space is similar to that outgassing from the Earth's interior. Neon, on the contrary, is kept entirely within the Earth's atmosphere. An explanation for the loss of gases to space is given by gas kinetics. In order to overcome the Earth's gravitation a molecule needs to have a velocity of about 11 km/s. This is definitely more than the average speed of most molecules at the upper boundary of the atmosphere. The average speed of the gas molecules is mainly a function of the temperature, which is estimated to be approximately 1500 K in the upper atmosphere. Hydrogen (H_2) also has a relatively short lifetime and therefore a low abundance in the atmosphere. Furthermore, the hydrogen which is formed, e.g. by microbial activity, reacts with oxygen to form water which further decreases the hydrogens' concentration (Eq. 1).

$$2\,H_2 + O_2 \rightarrow 2\,H_2O \qquad\qquad \text{(Eq. 1)}$$

Solar UV radiation, however, can split water into free H-atoms, which are highly volatile. Fortunately, only few water molecules reach the stratosphere, where they are exposed to UV-radiation.

The universal solvent

Due to its polar character, water is a good solvent for salts, polar organic compounds and gases. Within the hydrological cycle water directly interacts with various solid phases, such as dust, soil, rocks, and living organisms. Thus, whatever has been in contact with water is reflected by the chemical make-up of water.

Water dissolves a variety of substances very effectively. This is one of the reasons why almost all biochemical reactions take place in aqueous solutions and why water is
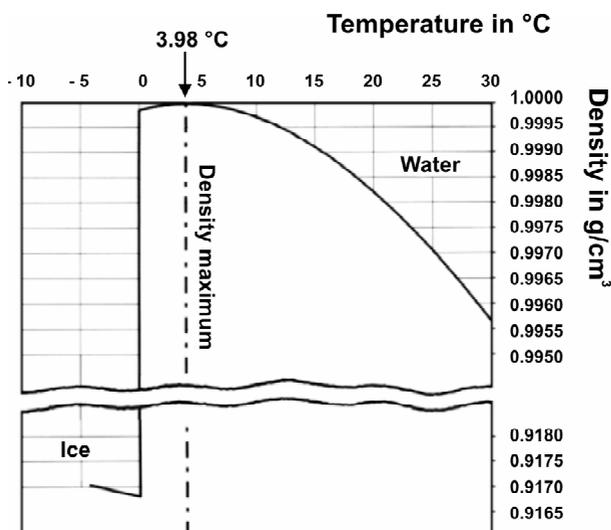

Fig. 1.2-3: Density of liquid water as a function of temperature.

indispensable as a reaction medium for all metabolic processes in living cells.

Solutions are homogeneous liquid phases consisting of two or more constituents. The extensive interactions among dissolved molecules and water molecules are characteristic for aqueous solutions. Depending on the type of substance dissolved, different interactions can be observed. This concerns the type of interaction as well as the repercussion arising from those interactions on water structure in the immediate surrounding of the solute.

Dissolution of salts (electrolytes)

Electrolytes are compounds which are able to conduct current through ionic migration. Thus, an aqueous electrolytic solution is formed if a substance XY dissociates in water according to

$$XY \rightarrow X^+ + Y^- \hspace{2cm} \text{(Eq. 2)}$$
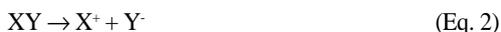
(The positive ions X^+ are called cations and the negative ones Y^- anions)

During the dissolution of electrolytes interactions between the ions of the electrolytes and the dipoles of water arise. This results in one of the most important effects observed concerning the dissolution; the so-called hydration. The hydration describes an attachment of polar water molecules onto dissolved ions. A primary hydration shell builds up around the ion and onto it further water molecules associate, however, with decreasing attachment strength; i.e. the intensity of interaction decreases from the central ion outwards.

The extent of hydration depends on the charge, i.e. valence, and the radius of the ion or the ratio of those two values. As a general rule, hydration of cations increases with increasing charge and decreasing radius. Anions are normally less hydrated than cations. The amount of attached water molecules is given by the hydration number, even though its determination remains highly difficult. Octahedral co-ordination occurs preferentially among many cations.

An example for the dissolution of electrolytes will be given by describing the dissolution of NaCl, simplified in *Fig 1.2-4.*

Once the NaCl crystal is in contact with water, water molecules interact with the surface of the crystal. Due to the polar nature of the water molecules, negative poles of water molecules attach to positive Na^+-ions and positive poles attach to negative Cl^--ions. This reaction is highly exothermic, i.e. it releases heat, because the hydration enthalpy of the ions is greater than their lattice energy.

Thus, the ion-ion bonds existing in the crystal structure are disrupted, and the ions are released from the structure into a dissolved phase where they occur as mobile, hydrated ions. The high dielectric constant of water prevents the formation of neutral molecules from ions with opposite charges. As the Coulomb force is inversely related to the dielectric constant, the electrostatic attraction between the ions is very low. The hydrated ions are responsible for the electric conductivity of the solution. Under the influence of an electric field, positively charged ions (cations) migrate towards the cathode (negative pole) and negatively charged ions (anions) towards the anode (positive pole). In the vicinity of the hydration complex, the normal structure of water is disturbed. In between the ordered hydration complexes and the disordered water, zones of a partly disrupted water structure can be found. The described interactions between electrolytes and water molecules as well as the high dielectric constant of water explain the high solubility of most electrolytes.

Some salts are able to enhance the water structure in aqueous solution (e.g. $Al_2(SO_4)_3$, $MgSO_4$), while others rather deteriorate it (e.g. NH_4Cl, KNO_3). *Table 1.2-3* shows typical specific conductivities of selected waters. The solubility products of some poorly soluble salts and hydroxides are given in *Table 1.2-4.*

Dissolution of organic substances

Most organic substances are non-electrolytes and occur as undissociated molecules in water. Polar and non-polar organic substances undergo different dissolution mechanisms.

Non-polar molecules such as hydrocarbons are incorporated into the intermolecular spaces that exist due to the tetrahedral configuration of water. In general, this process leads to an enhancement of the water structure. In the vicinity of dissolved molecules more hydrogen bonds exist than further away. This »enhanced« water structure results in a relatively low solubility of the non-polar organic substances. This is of practical importance regarding water pollution from crude oil, pesticides, pharmaceuticals and other xenobiotics. The concentrations of those dissolved substances are usually below the mg/L-range.
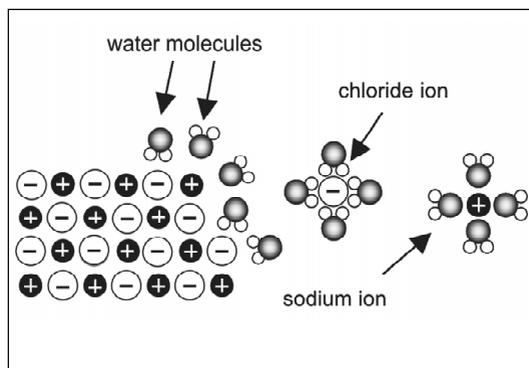

Fig. 1.2-4: Scheme of dissolution of a NaCl crystal.

Polar organic molecules consist of a non-polar part and a functional group, which is responsible for creating an asymmetrical charge distribution on the molecule, leading to a polar character. The effect of this functional group, with regard to the dissolution, is due to an active H-atom (proton donor function) or atoms with a free electron pair (proton acceptor function), both of which can participate in hydrogen bonds. *Table 1.2-5* shows some examples of such functional groups.

Polar substances, being able to form hydrogen bonds, exhibit similar properties as the water molecules themselves and can therefore associate with them (the principle of: similia similibus solvuntur – like dissolves like). This explains the high solubility of these compounds, which may proceed to complete miscibility. The more non-polar and bigger the organic rest R, however, is, the lower the solubility in water will be.

Dissolution of gases

As a consequence of ample contact between water and the atmosphere within the hydrological cycle, the components of the air, especially the gases nitrogen, oxygen and carbon dioxide, will dissolve in water. The solubility of gases in water can be described by HENRY-DALTON's law with sufficient accuracy in most applications:

$$c_i = K_H \times p_i \qquad \text{(Eq. 3)}$$

c_i = concentration of gas i in water in mol/m^3,
p_i = partial pressure of gas i in the gas phase in Pa,
K_H = HENRY-constant in mol/(m³×Pa).

DALTON's law states that in the equilibrium state the concentration of a gas in solution is proportional to the partial pressure of this gas above the solution. The HENRY-constant generally decreases with temperature resulting in a lower solubility of the gas. The less important dependence of the constant on pressure and salinity can be neglected for most practical calculations.

According to the law for ideal gases, the partial pressure p_i of a gas is the product of the partial volume of the gas and the total pressure. The concentration c_i in water can then be calculated in an equilibrated state by using the partial pressure p_i. The resulting concentration is given in the units of mol/m³. In order to convert this result into the more frequently applied units of g/m³ ($=$ mg/L), the concentration has to be multiplied by the molar mass M_i of the dissolved gas i.

In dry, air nitrogen, oxygen and carbon dioxide have partial pressures of 7.803×10^4 Pa, 2.099×10^4 Pa and 0.003×10^4 Pa, respectively. The resulting solubilities at 20 °C for those gases are given in *Table 1.2-6*.

Table 1.2-3: Specific conductivity of selected waters (according to BENDLIN 1995).

Water	κ in µS/cm
Ultrapure water	0.055
Demineralized water	0.1 ... 1
Drinking water	30 ... 2,000
Brackish water	20,000 ... 1,000,000
Lake Constance water	322
Groundwater, Munich	537
Bank filtrate, river Rhine nearby Düsseldorf	702

Table 1.2-4: Solubility products of some poorly soluble electrolytes.

Electrolyte	Solubility product
$CaSO_4 \cdot 2\,H_2O$	2.5×10^{-5} (mol/L)^2
$MgCO_3$	1.3×10^{-5} (mol/L)^2
$Ca(OH)_2$	8.0×10^{-6} (mol/L)^3
$CaCO_3$	4.8×10^{-9} (mol/L)^2
$AgCl$	1.6×10^{-10} (mol/L)^2
$FeCO_3$	2.1×10^{-11} (mol/L^2
$Mg(OH)_2$	5.5×10^{-12} (mol/L)^3
$Al(OH)_3$	1.0×10^{-33} (mol/L)^4
$Fe(OH)_3$	1.0×10^{-38} (mol/L)^4

Table 1.2-5: Functional groups and number of their proton donor (PD) or proton acceptor (PA) sites.

Group (compound)		PD	PA
Water	H—ŌH	2	2
Hydroxyl-	R—ŌH	1	2
Carbonyl-	R_2C=Ō	0	2
Carboxyl-	R—C(O)(OH)	1	4
Amino- (primary)	R—N̄H$_2$	2	1
Amino- (secondary)	R_2N̄—H	1	1
Amino- (tertiary)	R_3N|	0	1

Table 1.2-6: Water solubility of the main components of air at 20 °C.

Gas	K_H (20 °C) mol/(m³× Pa)	Volume fraction in the air (%)	Amount conc. in water (mol/m³)	Mass conc. in water (g/m³)	Volume fraction in dissolved air (%)
N_2	0.691×10^{-5}	78.03	0.539	15.09	64.3
O_2	1.366×10^{-5}	20.99	0.287	9.18	34.3
CO_2	38.66×10^{-5}	0.03	0.012	0.51	1.4

The values given in *Table 1.2-6* show that CO_2 dissolves relatively easily in water and that even oxygen is more soluble than nitrogen. This is of crucial importance for aquatic life.

Reaction diversity

The most important function of liquid water for life processes is its role as reaction medium for a great variety of soluble substances. Not only are they distributed, but they can diffuse towards and react with each other.

The reactions can be separated into:

• Acid-base reactions
• Redox reactions
• Complexation
• Sorption/desorption reactions
• Condensation/hydrolysis

During such reactions, either hydronium ions (H_3O^+), electrons (e^-) or electron pairs are transferred or water molecules are exchanged, and phase transitions (liquid/solid) occur. Additionally, many reactions are accelerated due to catalytic effects. This includes photocatalytical as well as biochemical transformations through enzymes.

One of the most important reactions is the autoprotolysis of water (Eq. 4):

$$2\ H_2O \leftrightarrows H_3O^+ + OH^- \qquad \text{(Eq. 4)}$$

Thermodynamically, the left side is favoured. The product of the ion activities a at 25 °C is:

$$K_w = a(H_3O^+) \times a(OH^-) = 10^{-14}\,(mol^2/L^2) \qquad \text{(Eq. 5)}$$

The pH, used for measuring the acidity, is defined according to Eq. 6:

$$pH = -\log_{10} a(H_3O^+) \qquad \text{(Eq. 6)}$$

Water, water, every where

The fundamental importance of water for life has influenced humanity at all times. This includes its essential function for life as well as the fascination and mystics which are derived from water. Water runs as a thread through human evolution. Its occurrence, availability, properties and behaviour, however, have become almost self-evident for us. We must counteract this development and re-establish an awareness of the uniqueness of water and of our responsibility for its sustainable usage ♦