Report

Water - its significance in science, in nature and culture, in world religions and in the universe

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2. Physical and Chemical Properties of Water
2.1 Phase Diagram, Water molecule, heavy Water and Clusters

**Basic structures in the three phases**

- **Gas**: H$_2$O molecules in the gaseous state (water vapour) at low gas pressures. The molecules are moving freely in space exhibiting translational- and rotational motions.

- **Liquid**: “Structure” of water molecules in liquid water: the molecules are linked by hydrogen bonds and are essentially disordered. The molecules exhibit hindered translational and rotational motions and at the same time the H–bridges are constantly broken and reformed.

- **Ice**: In “normal” hexagonal ice Ih, the oxygen atoms form an ordered hexagonal lattice, while the hydrogen atoms are distributed statistically. The identity of the molecules is, however, conserved (molecular crystal). The molecules are linked together by hydrogen bonds.
Phase diagram of Water

$T_p$: triple point at $T_p = 0.01 \, ^\circ\text{C}$ and $P_p = 611.657 \, \text{Pa} = 6.116 \times 10^{-3} \, \text{bar}$

$T_c$: critical point at $T_c = 374.12 \, ^\circ\text{C}$ and $P_c = 221.2 \, \text{bar}$

The numbers I, VI, VII and VIII denote different modifications of ice.
2.2 The Water Vapour

Water vapour: Water in the gaseous state

Clouds are water droplets

Water vapour in the air

Liquid water

$T_2 > T_1$

$P_2 > P_1$
Water molecules in the vapour

Individual molecules are flying in all directions with different velocities \( v \); the higher the temperature, the larger is the mean velocity \( <v> \). (Figure prepared by P. Brüesch).

The \( \text{H}_2\text{O} \) molecule

- **Bond angle** \( \alpha \):
  - 104.5° in vapour
  - 105.5° in water
  - 109.5° in ice
  - \( \alpha \neq 180° \) (!)

- **Nuclear distance or bond length**: \( d(\text{O-H}) \):
  - about 1 Ångström = 1 Å
  - 1 Å = 0.000'000'1 mm

- **Molar mass**: \( \approx 18 \) g

- **O-H bond**: strong electron pair - binding

- **H\(_2\)O and D\(_2\)O are polar molecules**: the centers of gravity of the negative and positive charges are separated!

- **Dipole moment** \( p \) (polar molecule)

- **Liquid H\(_2\)O is an excellent solvent for a large number of substances**!
The $\text{D}_2\text{O}$ molecule of heavy water

$\text{D} = \text{Deuterium}$:

Chemically, the $\text{D}_2\text{O} -$ molecule behaves as the $\text{H}_2\text{O} -$ molecule, however:

$\text{D}_2\text{O}$ is heavier than the $\text{H}_2\text{O} -$ molecule by a factor of $20/18 = 1.11$ → slower kinetics in metabolism!

Natural abundance of $\text{D}$:
about 0.02 % of $\text{H}$ → important for the origin of water on the Earth

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Heavy water: $\text{D}_2\text{O}$

In heavy water or deuterium oxide, $\text{D}_2\text{O}$, both hydrogen atoms are replaced by deuterium $\text{D}$. The nucleus of a $\text{D}$–atom contains one proton and one neutron.

Molar mass: $\approx 20$ g; Freezing point: 3.82 ºC, boiling point: 101.42 ºC, density at 20 ºC: 1.105 g/cm$^3$, (largest density: 1.107 g/cm$^3$ at 11.6 ºC), $\text{pH} = 7.43$.

Heavy water is produced by electrolysis of natural water which contains about 0.015 % deuterium; in the residue of the electrolyte, heavy water can be enriched up to more than 98 %. Pure heavy water is strongly poisonous. Because of its moderating power and small absorption for neutrons, heavy water is used as a moderator for nuclear reactions → production of slow neutrons!

In addition to $\text{D}_2\text{O}$ there exists also deuterium protium oxide, $\text{HDO}$, which sometimes is also called heavy water; in pure form it is unstable.

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Tritium oxide: $\text{T}_2\text{O}$

Tritium $\text{T}$ is the heaviest isotope of hydrogen: The nucleus of a $\text{T}$-atom is composed of one proton $\text{p}$ and of two neutrons $\text{n}$. For this reason the molar mass of Tritium oxide, $\text{T}_2\text{O}$, is $\approx 22$ g.

Freezing point of $\text{T}_2\text{O}$: 4.48 ºC, boiling point: 101.51 ºC: density: 1.2138 g/cm$^3$; $\text{pH} = 7.61$.

Since $\text{T}$–atoms are unstable and decompose gradually into helium atoms (half–life: 12.32 years), $\text{T}_2\text{O}$ is radioactive.

Due to its high diffusivity, $\text{T}_2\text{O}$ in its gaseous state is particularly dangerous for living beings. This is because exposition causes all organs uniformly with radioactive radiation.
The isotopes H, D and T

\[ H = ^1H \quad D = ^2H \quad T = ^3H \]

Hydrogen, Deuterium, Tritium

e: electron, p: proton, n: neutron; H, D, and T possess 1, 2 and 3 nucleons, respectively, in their nuclei.

Water, “intermediate heavy water” and “heavy water”

Hydrogen atom H

Deuterium - atom D

charges: e: -q, p: +q, n: 0

masses: \( m_p = m_n \gg m_e \)

The abundance of D in natural hydrogen H is very small, about 0.015 %.
Molecular orbitals of the $\text{H}_2\text{O}$ molecule

For the calculation of the electronic structure of molecules, quantum mechanics must be used (the electron is an elementary particle having a very small mass: $m_e = 0.9107 \times 10^{-27} \text{g}$ (!))

Result: 4 club-shaped “molecular orbitals” are formed where each of which is occupied by 2 electrons; they indicate the residence probability of the 4 electron pairs.

The electronic structure is not plain but rather 3-dimensional and the end points of the clubs form a tetradron (!)

Thermal Motion of a $\text{H}_2\text{O}$-Molecule

The atoms O and H fluctuate randomly about their equilibrium positions; this leads to small changes of the bond lengths and of the bond angle.

Approximate decomposition of thermal motion into three normal vibrations:

The normal modes of vibrations can be observed by Infrared and/or Raman spectroscopy.

In reality, the amplitudes of the atomic displacements are much smaller than illustrated; exception: Water vapour on the Umbra of the Sun at temperatures between 3000 and 3500 °C (s. p. 443).
Infrared Vibration – Rotation Spectrum of Water Vapour
Important for global warming !!

The fine-structure absorptions which are grouped around the fundamental vibrations originate from the rotational motions of the whole molecules.

From an exact analysis of the spectra it is possible to deduce the geometry of the molecules!

(Spectrum measured by P. Brüesch)

1 THz = $10^{12}$ Hz = 1 Billion Hz; 1 Hz = 1 vibration / second

The Water Dimer:

The positively charged proton $H^+$ links the negatively charged $O_1$ of the left hand sided molecule with the negatively charged atom $O_2$ of the molecule at the right hand side.

$O_1 \cdot H \cdot \cdot \cdot O_2$ is the hydrogen bond

The hydrogen bond (H-bridge) is nearly linear and $d(O_1 \cdot H \cdot \cdot \cdot O_2)$ is about 3 Å.
Remarks about Hydrogen Bonds

Hydrogen Bonds: General:

Hydrogen bonds (H– bonds), are chemical bonds of mainly electrostatic nature. In general, their bond strengths are distinctly lower than that of covalent or ionic bonds. The H– bonds are responsible for the fact that water molecules usually cluster to form larger groups. For this reason also warm water remains a liquid with a relatively high boiling point. This fact is a necessary prerequisite for most living beings. In proteins H– bonds glue the atoms together, thereby maintaining the three-dimensional structure of the molecules. H– bonds also keep together the individual ropes to form the characteristic double helix (s. pp 199–201; 4-A-5-1).

Hydrogen Bonds in Water:

H– bonds are responsible for a number of important properties of water! Examples are the liquid state at normal conditions, the large cohesion, the high boiling point and the density anomaly at 4 °C (pp 69, 73, 74). The typical bond length H–O of H– bonds in water is 0.18 nm and the total O–H–O bond is nearly linear and its length is about 0.3 nm (1 nm = 10⁻⁹ m = 10 Å (Angström)) (see pp 26, 39, 41).

In liquid water, preferentially 4 water molecules are linked together with a central molecule (s. pp 60, 61). During vaporazation these H– bonds must be broken; this also explains the relatively high vaporization energy at 100 °C.

It has been found by means of Compton scattering that the covalent O–H bonds of a water molecule partly extend into the weak H–O bonds. Therefore, although the H– bonds are essentially ionic they possess a small covalent contribution.

Clusters of H₂O: 1) Dimer and Hexamer

The formation of H– bonds in water is cooperative: The formation of a first H– bond triggers a change of the charge distribution of the molecules in such a way that the formation of a second H– bond is favoured. This leads to the formation of clusters.

Simplest picture: H– bonds are purely electrostatic, meaning that the incompletely screened positive charge of the proton is attracted by the negative charge of the “ion–pair” electrons.

However, Compton scattering by a low–pair electron (two small circles) of the water molecule to the right shows: The covalent O–H bonds (dark-yellow clouds) extend into the H– bonds (bright-yellow clouds). Therefore, the H– bonds are partly covalent as predicted by Linus Pauling (1935!).

E.D. Isaacs et al., PRL 82, 600 (1999).

The experiment has been performed on ice.
In contrast to the dimer, the clusters with \( n > 3 \) are only weakly polar or even non-polar, such that the permanent dipole moment \( m \) is small or even zero.

As shown in the model, the six–sided ring is not plane!

The water hexamer is the smallest particle of the hexagonal ice.
Clusters of H₂O: Cyclic and Tetrahedral Pentamers (H₂O)₅

Examples: n = 5: Pentamer (H₂O)₅

General: a (H₂O)ₙ-cluster is a group of n water molecules, which are linked together by hydrogen bonds.

Two other compounds with Hydrogen bonding

Hydrogen fluoride is composed of HF molecules. Because of the difference in electronegativity between H and F, a hydrogen bond occurs between the hydrogen atom of a molecule and the fluorine atom of a neighbouring molecule. The acid is an extremely corrosive liquid and is a strong poison.

Liquid Ammonia, NH₃, is a very good solvent and exhibits similar properties as H₂O; it is, however, considered a high health hazard. N and H of neighbouring molecules are linked by H-bonds.
2.3 The Ices of Water

Depending on temperature and pressure as well as on the preparation conditions, there exist a large number (at least 13) of stable and metastable crystalline ices.

- Structural building stone: tetrahedral coordination with hydrogen bonds between the molecules.

- The phase diagram is determined by the Clapeyron equation:

\[ \frac{dP}{dT} = \frac{\Delta H_m}{T \Delta V_m} \]

The temperature and pressure regimes associated with most of the 13 known crystalline phases are indicated here. When hexagonal ice at 77 K is subjected to increasing pressure, so-called amorphous ice forms: at 1 GPa (blue circle), high-density amorphous ice forms; if the temperature is then raised, very-high-density amorphous ice forms (red circle).
Ices at low temperatures
1. „Normal“ hexagonal ice (ice Ih) with proton disordering
2. Ordered hexagonal ice XI
3. Cubic ice Ic
4. Glassy and/or amorphous ice

Ices at intermediate temperatures
5) ice II: a structure with ordered protons
6) metastable ice III and proton-ordered structure ice IX
7) metastable ice IV and monoclinic ice V
8) tetragonal ice XII

Ices at high pressures
9) ice VI: tetragonal unit cell; density $= 1.31 \text{ g/cm}^3$ (-175°C, 1 bar)
10) ice VII: bcc–lattice of O–atoms; H–atoms disordered; density $= 1.599 \text{ g/cm}^3$
11) ice VIII: is formed by cooling of ice VII; protons are ordered; density $= 1.628 \text{ g/cm}^3$.
12) ice X: is formed from ice VII by increasing the pressure to 165 GPa = 1.65 Megabar!
   Here, the protons are located midway between two neighbouring oxygen atoms! This
   means that ice ceases to be a molecular crystal $\rightarrow$ atomic crystal (s. p. 56)!

Modifications of Ice - 2

• Depending on temperature and pressure, there exist different modifications of ice, which differ in their structures, i.e. in their spatial distributions of the H$_2$O–molecules.

• up to now there are at least 13 modifications: ice Ih, ...... ice XII

• our “natural” ice: ice Ih (h = hexagonal)

• “metastable” ice: such as ice XII (about -40°C, 4000 bar)

• exotic “glowing ice”: such as ice VII, ice X (about 500°C, 100000 bar)
  (see glowing ice in Jupiter (p. 475) and in Saturn (p. 480).

• Superionic conducting ice (very high mobility of the protons!)

• metallic ice?
Structure of Hexagonal Ice Ih

Hexagonal structure of ice Ih:
each H$_2$O-molecule is surrounded by 4 nearest H$_2$O-molecules (●).
red line: H-bonds

Head with potbelly: O-atom
hands: H-atom
lags with feed: H–bridges;

note the 6-fold ring of O-atoms

Philip Ball: “H$_2$O: A Biography of Water”
Weidenfeld & Nicolson (1999), p. 159

Far–Infrared and Infrared Spectrum of Ice Ih

Absorption (cm$^{-1}$)
Frequency (THz)

vibrations and rotations of the whole molecule

symmetric and antisymmetric vibrations of the O–H bonds

hindered rotations (librations) of the molecules

bending motion H–O–H

overtones

The corresponding spectrum of liquid water is shown at pp 114 and 115.

There exist two low-frequency “external” vibrations of the whole molecules and 3 high-frequency “internal” vibrations $\nu_1, \nu_2, \nu_3$, of the atoms within the molecules.
Snow crystals are art works!

Note the approximate hexagonal symmetry of the crystals! (s. p. 176-178 and Ref. R.4.3.6)

The seven basic forms of snow crystals, each of which possesses hexagonal symmetry (s. p. 176)
The Ice Grotto of the Rhone Glacier

Note the phantastic blue colours!
(Photo from Dr. Martin Carlen in: “Der Rhonegletscher und seine Eisgrotte” (2003))

Because of global warming, the existence of the Ice Grotto is more and more in danger!!

Ice VII, Ice VIII and Ice X

Phase diagrams of the two high-pressure modifications of ice VII and ice VIII:

Their phase boundaries have been detected by means of Raman scattering (empty squares: H₂O, full squares: D₂O).

The oxygen atoms are green, the hydrogen atoms are red.

The structure of ice VIII is hexagonal with ordered protons; by heating, it transforms into the cubic form ice VII with disordered protons.

In cubic ice VII each oxygen atom is tetrahedrally surrounded by four hydrogen atoms and the molecules are linked by O–H–O bonds.

If the pressure is increased up to 165 MPa, there is evidence for the formation of a new structure in which the hydrogen bonds disappear. In this structure, ice X, the mean positions of the hydrogen atoms are in the centers between the two oxygen atoms. This means that in ice X there exist "symmetrical" O–H–O bonds which implies that we are dealing with an atomic crystal rather than with a molecular crystal.

1 Gpa = 10 000 bar
Temperatur (K)
Pressure (GPa)
At extremely high pressures, a fundamental change of the structure of normal water–ice occurs: A particularly dense ice is formed, in which the strong covalent bonds within a water molecule and the weak hydrogen bonds between the water molecules become equivalent. The pressure at which this occurs as well as the detailed formation of this process has been studied by an international research team guided by Prof. Dominik Marx (Lehrstuhl für Theoretische Chemie der Ruhr–Universität Bochum (RUB)) by means of theoretical model calculations (see Ref. R.2.3.9).

Sophisticated quantum mechanical computer simulations of the experiments at room temperature are able to show in detail of how molecular ice is transformed into ice X, demonstrating the transition of hydrogen bonds and covalent bonds into atomic bonds as a result of high external pressures. This occurs via a form of ice, in which the hydrogen atoms have essentially lost their memory as to which of the two oxygen atoms they belong with the consequence that they are permanently oscillating between their two oxygen neighbours. This corresponds to a very dynamical form of ice, which does not obey anymore the famous „ice–rules” of Linus Pauling as proposed around 1930.

Other scientists have speculated, that these unconventional forms of „hydrogen bonds” which are formed in ice at high pressures, could play an important role in processes such as in enzyme catalysis in which hydrogen bonds and transfer mechanisms from H–O-----H to H–O–H bonds play an important role in biochemical processes.
2.4 Liquid Water: Structure and Dynamics

“Random Network” Model of liquid water

“Groundstate”: totally interconnected “Random Network” having an open tetrahedral structure; realized in superercooled water.

“Excited state”: macroscopically interconnected “Random Network” containing many deformed and broken bonds; continuous topological reorganization; realized in the stable state of water.

Anomalous properties: as a result of the competition between “open” water (as in ice) and more compact regions with deformed and broken hydrogen bonds. (C.A. Angell: J. Phys. Chem. 75, 3698 (1971); F. Stillinger, Science 209, 451 (1980)).

“Random Network Model” with tetrahedral coordination (only the O– atoms are shown). Originally, the model has been constructed for Si and Ge. F. Wooten and D. Weaire in: Solid State Physics 40, pp 1-42 (1987).
Mean instantaneous configuration of a water molecule

The O⋯H - O hydrogen bonds are usually bent or broken but are reformed continuously and quickly.

The lifetime of a hydrogen bond is very short, only about a billion of a second, i.e. about $10^{-12}$ seconds; this is a time in the picosecond (ps) range or less.

More compact and much more dynamic structure as in ice!!

Ballet of H$_2$O – Molecules in Liquid Water

Water molecules – with hands re-presenting lone pairs of electrons – perform a wild dance that involves grabbing neighbours by the ankles. These clasps, due to hydrogen bonding, lead to a tetrahedral arrangement of neighbours around each molecule.

This is the central motif of the structure of water, and the key to all its anomalous properties.

Liquid water has a very large specific heat:
1 cal / (g °C) ! → buffer for stabilization of clima!!

Figure and text by: Philip Ball: “A Biography of Water”, p. 159;
The Figure has been slightly modified by P. Brüesch by adding the blue and green arrows indicating the exchanges and rotations of the molecules.
In ice, the molecules execute small vibrations around their equilibrium positions located at a regular lattice.

For the calculation of the molecular dynamics, realistic interaction forces between the molecules are introduced which simulate the nature of hydrogen bonds.

Result: In liquid water the molecules execute a wild dance. They are still loosely connected by hydrogen bonds but these bonds are no longer straight lines as in ice but are rather strongly tilted and break very easily. As a consequence, partners exchange very wildly and rapidly with a mean residence time of the order of billionths of seconds!

In a rough first approximation, this irregular motion can be decomposed into several fundamental vibrational and librational motions (see pp 64, 65).

Local structure of liquid water

Disordered structure of liquid water: a snapshot from a molecular dynamics study (s. p. 62)

The dashed white lines indicate the hydrogen bonds between neighbouring water molecules.
**“Internal” molecular vibrations:**

- $v_1$
- $v_3$
- $v_2$

**“External” molecular vibrations:** “librations”

- Hindered translation: $v_t$
- Hindered rotation: $v_r$

If an infrared frequency coincides with a molecular vibration, resonance occurs at this frequency by absorbing a large portion of the infrared light $\Rightarrow$ infrared – absorption - band

Absorption spectrum in the Far – Infrared of the intermolecular vibrations of liquid water at 27 °C. In a rough approximation, the wild dance of the water molecules (pp 61 - 62) can be decomposed into two fundamental vibrations. These absorptions can be observed as two broad absorption bands at 675 cm$^{-1}$ (about 20 THz) and near 200 cm$^{-1}$ (about 5 THz). The broad and intensive band near 675 cm$^{-1}$ can be assigned to the „hindered“ rotational motion of the H$_2$O – molecules, while the band near 200 cm$^{-1}$ is due to the „hindered“ translational motion of the H$_2$O – molecules. The extremely large widths of these absorption bands are due to the complex interactions between the H$_2$O – molecules (distribution of absorption frequencies !). The two „external“ normal vibrations are illustrated at page 64 and the complete infrared spectrum is shown at page 114. (The above Figure has been composed by P. Brüesch).
2.5 Liquid Water: Anomalies

- Liquid water is about 9% heavier than ice!
- The density maximum of water is not at the freezing point at 0 °C but lies at about 4 °C!
- The melting temperature decreases with increasing pressure!
- Compared with other substances, the heat capacity, the surface tension and the thermal conductivity are unusually large!
Anomalies : General - 2

• For a large number of substances, water is an excellent solvent (s. pp. 127 - 135)!

• Pure liquid water can be supercooled down to as low as -37 °C without freezing!

• If supercooled and cold liquid water is heated up until 4 °C it exhibits a contraction!

Note: both, supercooled and superheated water are very important in nature!
(Example: metastable superheated water present in the xylem conduits of high trees (pp 215, 216; 220, 221)

Four additional Anomalies

Temperature dependences of a) the density $\rho$; b) the thermal expansion coefficient $\alpha_T$; c) the isothermal compressibility $\kappa_T$, and d) the isobaric specific heat $C_p$ at 0.1 MPa. The red curves indicate the experimental data for Water (s. Ref. R.2.0.17, R.2.5.3). The blue lines indicate the behaviour for simple liquids (Annotation of axis redrawn)
With increasing pressure the melting temperature increases.

With increasing pressure the melting temperature decreases!
2.6 Densities and specific heat

At the transition from water to ice the density decreases by about 9% !!

Anomaly: ice is lighter than water !!!
The Density Maximum of Water is at $4^\circ C$!

<table>
<thead>
<tr>
<th>Temperature ($^\circ C$)</th>
<th>Density (g / cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00000</td>
</tr>
<tr>
<td>2</td>
<td>0.99992</td>
</tr>
<tr>
<td>4</td>
<td>0.99984</td>
</tr>
<tr>
<td>6</td>
<td>0.99976</td>
</tr>
<tr>
<td>8</td>
<td>0.99969</td>
</tr>
<tr>
<td>10</td>
<td>0.99963</td>
</tr>
</tbody>
</table>

Maximum density at $4^\circ C$

Anomaly: by cooling below $4^\circ C$ the density decreases again!

For nearly all other liquids (except Bi) the density increases with decreasing temperature down to the melting point.

Density of Water in its whole Range of Existence

- TMD = Temperature of Maximum Density
- Pressure $P = 1$ bar

Supercooled region

Stable region

Superheated region

TMD = $4^\circ C$
Specific heats $C_p$ : Comparison with liquid water

$C_p$ of liquid water: about two times larger than that of ice Ih at $T_S$ and than that of vapour at $T_D$. Reason: deformation and/or dissociation of hydrogen bonds which give rise to a large and strongly temperature dependent configurational energy.

At $T_S$ and $T_D$, energy is used for melting and evaporation, respectively, leading to sharp “lambda – anomalies” of $C_p$ ($\lambda$ – anomalies at $\uparrow$).

(Figure composed by P. Brüesch from several experimental Data)
Specific Heat of Liquid Water in its whole range of Existence

\[ C_p = \frac{(\partial H/\partial T)_p}{(\partial S/\partial T)_p} = T \left( \frac{\delta S}{\delta T} \right)_p \]

Remarks about the anomalies of the temperature dependence of the specific heat \( C_p(T) \), of the thermal expansion \( \alpha(T) \) and of the isothermal compressibility \( \kappa(T) \) of liquid water.

For typical liquids, \( C_p \) decreases slowly with decreasing temperature and this is also the case for liquid water but only down to 35 °C. At 35 °C the specific heat of water passes through a minimum and increases again with decreasing temperature (p. 77).

In the supercooled state, below 0 °C, \( C_p \) increases strongly with decreasing temperature (p. 77).

Anomalous behaviours are also observed for the thermal expansion \( \alpha(T) \) (pp. 69 and 81) as well as for the isothermal compressibility \( \kappa(T) \) (pp. 69 and 82).

All three quantities, \( C_p(T) \), \( \kappa(T) \) and \( \alpha(T) \), behave in such a way as to suggest the existence of a singularity at low temperatures (below about -40 °C), but there is no proof for this conjecture. Although there exist a large number of theoretical models for the very unusual properties of water, these and many other anomalies remain essentially a puzzle.

Although it is often possible to explain one of the anomalies with an appropriate theoretical model, most other anomalies can not be explained with the same model. There exists no universal theory of liquid water!

It can, however, taken for granted that for the explanation of all anomalies, the complicated nature of the hydrogen bonds plays a central role.
Reason and Relevance of water’s high specific heat

Between 0°C and 100°C the specific heat of water is about 1 cal/(g°C). Compared with most other substances, the specific heat of water is therefore unusually high (see pp 75 and 77).

We can trace water’s high specific heat, like many of its other properties, to hydrogen bonding. Heat must be absorbed in order to break hydrogen bonds, and heat is released when hydrogen bonds form. A calorie of heat causes a relatively small change in the temperature because most of the heat energy is used to disrupt hydrogen bonds before the water molecules can begin moving faster. And when the temperature of water drops slightly, many additional hydrogen bonds form, releasing a considerable amount of energy in the form of heat.

What is the relevance of water’s high specific heat to life on Earth? By warming up only a few degrees, a large body of water can absorb and store a huge amount of heat from the sun in the daytime and during summer. At night and during winter, the slow cooling down of water stabilizes the temperature of the air. Thus because of its specific heat, the water that covers most of the planet Earth keeps temperature fluctuations within limits that permit life. Also, because organisms are made primarily of water, they are more able to resist changes in their own temperatures than they were made of a liquid with a lower specific heat.
2.7 Various physical quantities and properties

Expansion coefficient $\alpha(T)$ of liquid water in its whole range of existence at 1 bar


(Figure compiled by P. Brüesch)
Isothermal compressibility $\kappa(T)$ of liquid water in its range of existance at $P = 1$ bar

\[ \kappa = -\frac{1}{V} (\partial V/\partial P) \]

![Graph showing isothermal compressibility vs. temperature]

**Normal region**

**Superheated**

**Supercooled**

$T_{\text{min}} = 46^\circ C$


(Figure compiled by P. Brüesch)

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**Thermal conductivity of Ice, Water and Vapour**

![Graph showing thermal conductivity vs. temperature]

At the transition from water to ice, the thermal conductivity increases by about a factor of 3.6; however, going from water to its vapour at the boiling point, the thermal conductivity decreases by about a factor of 27.

(Figure compiled by P. Brüesch)
At constant pressure, the viscosity decreases almost exponentially with increasing temperature; this behaviour is also found in the supercooled state. The temperature dependence of the viscosity can be approximated by

$$\eta(T) = \eta_0 \exp\left(\frac{\Delta E_h}{R \cdot T}\right) .$$

$\Delta E_h$ is the Arrhenius activation energy for viscous flow; at 0 °C, $\Delta E_h$ is about 5 kcal/mol. For water, the temperature dependence of $\Delta E_h$ is considerably stronger than for most other liquids.

For most liquids, $\eta$ increases strongly with increasing pressure $P$. This is also the case for water above 30 °C. Below 30 °C, however, the viscosity of water first decreases with increasing pressure, then passes through a minimum between $P = 1000$ to 1500 kg/cm², and only at higher temperatures it increases again.

In contrast to many other properties of water (such as the density, expansion, compressibility and specific heat), the surface tension does not show any obvious anomaly by cooling down into the supercooled state. In particular, no drastic increase is observed in the deeply supercooled state, i.e. no indication of an anomaly is observed by approaching -45 °C.

If the surface tension is not measured at 1 atm but rather along the boiling point curve, (s. pp 99 - 101), it decreases continuously and disappears at the critical point $P_k$ (354.15 °C and 221.2 bar). In other words, the miniscus of water in a glass capillary disappears at the critical point $P_k$.

One anomaly of water is the fact that it has the highest surface tension of all non-metallic liquids! This is due to the strong cohesion between water molecules as a result of hydrogen bonding.
Water striders (Wasserläufer) are walking on water. Due to the very high surface tension of water (s. p. 85), the water surface acts like an elastic film that resists deformation when a small weight is placed on it. In the present picture, two Water striders are mating on the Water surface, thereby producing a mirror reflection.

Mirror reflection of two water–striders during mating

The “Water - ions” H₃O⁺ and HO⁻ in ultrapure Water

Example: the dimer

Self – dissociation or self – ionization of pure water

hydroxide - ion OH⁻

hydronium - ion H₃O⁺

exchange of the O–H bond with the H------O bond

considering a given H₂O - molecule , a H₃O⁺ - ion is formed after about 11 h .

⇒ very seldom process !

In pure water at 25 °C there will exist about one H₃O⁺ ion and one OH⁻ ion in 550 millions of H₂O molecules ⇒ pH = 7

pH ≈ - log [ H₃O⁺ ] [ H₃O⁺ ] in mol / dm³

Self – dissociation or self – ionization of pure water

In pure water at 25 °C there will exist about one H₃O⁺ ion and one OH⁻ ion in 550 millions of H₂O molecules ⇒ pH = 7

pH ≈ - log [ H₃O⁺ ] [ H₃O⁺ ] in mol / dm³
Formation and Hydration of Hydronium - ions $\text{H}_3\text{O}^+$

Mechanism of formation of a hydronium ion $\text{H}_3\text{O}^+$ and of a hydroxide ion $\text{OH}^-$ (schematic representation of a proton - transfer)

In a dilute acidic solution, the small $\text{H}_3\text{O}^+$ ion is strongly hydrated: it is hydrogen-bonded to three $\text{H}_2\text{O}$ molecules forming a (H$_9$O$_4$)$^+$ ion complex. A similar complex exists for the $\text{OH}^-$ ion.

$2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$

pH of pure water and $\text{H}_3\text{O}^+$ ion concentrations as a function of temperature

With increasing temperature the pH decreases, i.e. the self–ionization $2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$ increases strongly as shown in the Table below.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>pH</th>
<th>$[\text{H}_3\text{O}^+]$ in $10^{-7}$ mol/L</th>
<th>number of $\text{H}_3\text{O}^+$ ions number of $\text{H}_2\text{O}$ molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.49</td>
<td>0.32</td>
<td>5.75 x 10$^{-10}$</td>
</tr>
<tr>
<td>10</td>
<td>7.27</td>
<td>0.54</td>
<td>9.70 x 10$^{-10}$</td>
</tr>
<tr>
<td>20</td>
<td>7.08</td>
<td>0.83</td>
<td>14.9 x 10$^{-10}$</td>
</tr>
<tr>
<td>25</td>
<td>7.00</td>
<td>1.00</td>
<td>18.0 x 10$^{-10}$</td>
</tr>
<tr>
<td>30</td>
<td>6.92</td>
<td>1.20</td>
<td>21.6 x 10$^{-10}$</td>
</tr>
<tr>
<td>40</td>
<td>6.77</td>
<td>1.70</td>
<td>30.6 x 10$^{-10}$</td>
</tr>
<tr>
<td>50</td>
<td>6.63</td>
<td>2.34</td>
<td>42.2 x 10$^{-10}$</td>
</tr>
<tr>
<td>100</td>
<td>6.14</td>
<td>7.24</td>
<td>130.4 x 10$^{-10}$</td>
</tr>
</tbody>
</table>
pH and normalized hydronium ion concentration as a function of T

With increasing temperature, the pH-value of pure water decreases. This does not mean that water becomes more acidic as the temperature increases; this decrease is rather due to the fact that with increasing temperature the self-dissociation of H₂O molecules:

\[ 2 \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^- \]

increases which results in a higher concentration of water ions. Note that at 25°C the pH = 7.

The Figure shows the ratio of the concentrations of H₃O⁺-ions and of water molecules in pure water as a function of temperature T, \( r_+ (T) = [\text{H}_3\text{O}^+] / [\text{H}_2\text{O}] \). \( r_+ \) increases with increasing T as does the ratio \( r_-(T) = [\text{OH}^-] / [\text{H}_2\text{O}] \) of the hydroxide ions OH⁻. Since \( r_+(T) = r_-(T) \), water remains neutral.

At 25°C, \( r_+ = r_- = 10^{-7} \text{ (mol/L) / 55.5 (mol/L)} = (10^3 / 55.5) \times 10^{-10} = 18 \times 10^{-10} \); [one mole of water has a mass of \( \approx 18 \text{ g} \)].

Mobilities of H₃O⁺- and OH⁻- ions as a function of temperature

\[ u = u(\text{H}_3\text{O}^+) + u(\text{OH}^-) = \sigma / (F \times c) \]

\( \sigma \) = measured conductivity (s.p 92), \( F \) = Faraday constant, \( c \) = concentration of H₃O⁺ - ions (or OH⁻ - ions), which are obtained from the observed ion product \( K_w \) of pure water at room temperature. Assumption:

\[ u(\text{H}_3\text{O}^+) = 0.64 \times u \]

\[ u(\text{OH}^-) = 0.36 \times u \] independent on temperature. The factor 0.64 has been deduced from the known mobilities \( u(\text{H}_3\text{O}^+) \) and \( u(\text{OH}^-) \) at 25°C.

(Figure prepared by P. Brüesch from different Data)
Temperature dependence of ionic conductivity $\sigma_{DC}(T) = q \cdot c(T) \cdot u(T)$ of ultrapure water at 1 bar. $u(T)$ is the total ionic mobility (s. p. 91).

At 25 °C chemically pure water has a pH-value of 7 and an extremely small specific resistance of $14.09 \times 10^6 \, \Omega \cdot \text{cm}$ which corresponds to a specific conductivity of about $70 \times 10^{-9} \, (\Omega \cdot \text{cm})^{-1}$ (s. p. 92). This very high resistivity results from the very small concentration of the $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions (about 1.5 ppb at 25 °C).
Pressure dependence of the ionic conductivity of pure water

red curve: at 30 °C; blue curve: at 75 °C

The values have been normalized to the known conductivity values at 1 atm.
Note the anomalous increase of the conductivity with increasing pressure!

The electric double layer at a metal electrode in pure water

Peter Brüesch and Thomas Christen: J. Applied Physics, 95, No 5, 2004, p. 2846 - 2856

Pure water is a weak electrolyte that dissociates into hydronium ions and hydroxide ions. In contact with a charged electrode, a double layer forms for which neither experimental nor theoretical studies exist, in contrast to electrolytes containing extrinsic ions like acids, bases, and solute salts. Starting from a self-consistent solution of the one-dimensional modified Poisson–Boltzmann equation, which takes into account activity coefficients of point-like ions, we explore the properties of the electric double layer by successive incorporation of various correction terms like finite ion size, polarization, image charge, and field dissociation. We also discuss the effect of the usual approximation of the average potential as required for the one-dimensional Poisson-Boltzmann equation, and conclude that the one-dimensional approximation underestimates the ion density. We calculate the electric potential, the ion distributions, the pH-values, the ion-size corrected activity coefficients, and the dissociation constants close to the electric double layer and compare the results for the various model corrections.
2.8 Phase diagram of Water

Phases of a single substance - 1

Depending on temperature $T$ and pressure $P$ it is possible that:

- A compound can exist in the solid, liquid or gaseous state
- Two or three states can coexist:
  - Solid $\leftrightarrow$ liquid: melting curve
  - Solid $\leftrightarrow$ vapour: sublimation curve
  - Liquid $\leftrightarrow$ vapour: vapour pressure curve
  - Solid $\leftrightarrow$ liquid $\leftrightarrow$ gas: triple point
• Two coexisting states are said to be in dynamical equilibrium if an equal number of molecules is transferred from state 1 into state 2 per unit time.

Solid ↔ liquid ↔ vapour ↔ : triple point

• The vapour pressure curve extends from the triple point up the critical point.

• Above the critical point it is no longer possible to distinguish between the liquid and gaseous state.

• liquid water can be supercooled!

• liquid water can be superheated!

Phases of a single substance - 2

Phase diagram of H₂O (schematic)

(*) : Ref. R.2.1.1, (p. 150)
Phase diagram of water

melting curve
melting point or freezing point at 1 atm and 0 °C
triple point: $T_{tr} = 0.098 \, ^\circ C$, $P_{tr} = 0.006 \, \text{bar}$
sublimation curve

$T_c = 374 \, ^\circ C$, $P_c = 221 \, \text{bar}$
boiling point curve
boiling point at 1 atm and 100 °C

Boiling point curve of water

critical point: $(374 \, ^\circ C, 221 \, \text{bar})$
triple point: $T_{tr} = 0.01 \, ^\circ C$, $P_{tr} = 611.73 \, \text{Pa}$
For each gas there exists a well defined temperature, above which it is impossible to liquify it at arbitrary high pressures. This temperature is known as the critical temperature $T_c$ of the gas. If the gas is cooled down to this temperature, it is possible to liquify it by application of a sufficiently high pressure. At the critical temperature $T_c$ a certain pressure is necessary, which is called the critical pressure $P_c$. For water, the critical point is at $T_c = 374$ °C and $P_c = 221$ bar.

Water above the critical point is called supercritical water (s. p. 99). Above the critical point, the densities of water vapour and liquid water are indistinguishable; for this reason, this state is called „supercritical“. Chemically, supercritical water is particularly active. For this reason, experiments have been performed to neutralize strongly harmful substances with the help of supercritical water. Examples include the hydrolytical decomposition of Dioxins and PCBs which are highly toxic chemicals.

Remarks to the critical point

(pp 99 – 101)

Superheated states of water

1 at = 1 kp / cm²

103
Pressure dependence of melting and boiling point

a) Water defines the temperature scale of Celsius

The Celsius scale is a temperature scale, defined such that (at normal pressure of 1013.25 hPa = 1 atm) water freezes at 0 °C and boils at 100 °C.

b) The melting point or freezing point of pure water is 0 °C. The melting point depends only very weakly on pressure. A prominent anomaly of water is, however, the fact that as the pressure increases, the melting point decreases (s. Figures at pp 70 and 99); at a pressure of 2000 bar, water freezes at a temperature as low as -22 °C.

c) The boiling point of a substance is the temperature, at which the vapour pressure is equal to the pressure of the surrounding atmosphere. At a pressure of $p_a = 1013.25$ hPa, water boils at 100 °C. The boiling point of water depends strongly on the external pressure (s. pp. pp 70, 99 - 101) and hence at the Earth from the altitude $H$ above the Sea level (see left-hand Figure): the boiling point decreases about 3 °C for every 1000 m increase in height. At the Sea level, $p_a = 1$ bar and on top of the Mount Everest with $H = 8850$ m (right-hand Figure), the Boltzmann barometric equation gives the result that the air pressure decreases according to the exponential law $p(H) = p_a \times \exp(-H / 7990)$ m) $= 0.335$ bar.

\[
BP(H) = 100 - 0.00304 \times H
\]

- Mt Everest: $H = 8850$ m $\Rightarrow$ BP $\approx 74$ °C $\Rightarrow$ air pressure $p(H) \approx 0.335$ bar

<table>
<thead>
<tr>
<th>Altitude H (m)</th>
<th>Boiling point BP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>2000</td>
<td>97.1</td>
</tr>
<tr>
<td>4000</td>
<td>94.1</td>
</tr>
<tr>
<td>6000</td>
<td>91.1</td>
</tr>
<tr>
<td>8000</td>
<td>88.1</td>
</tr>
<tr>
<td>10000</td>
<td>85.1</td>
</tr>
</tbody>
</table>

Example: Pressure cooker

- Pressure gauge: 0 to 1.6 bar excess pressure
- Thermometer: 0 to 150 °C
- Rule of thumb: $\Delta T = 10$ °C $\Rightarrow$ cooking time is 2 to 3 times shorter!
Schematic representation of the phases of water at different temperatures and atmospheric pressure

- **Superheated water**
- **Boiling point**
- **Stable (normal) water**
- **Melting point**
- **Supercooled water**
- **Here, water is stable only in its solid crystalline phase**
- **Ultraviscous water**
- **Glassy water**

**P – T Phase diagram of water**

(s. p. 106 for atmospheric pressure)

**Supercooled water**: Is obtained by careful cooling of very pure water.

„No man’s land“: Here, no liquid phase but only a solid crystalline phase exists (s. also p. 106)

„Glassy water“: If liquid water is very rapidly cooled down, a glassy amorphous ice is formed.
LDA: „Low - Density Amorphous“ ice
HDA: „High - Density Amorphous“ ice

Deeply undercooled liquid water**: If LDA at atmospheric pressure (= 0.1013 MPa = 1013 hPa) is heated above -137°C, then a highly supercooled liquid water is produced: deeply supercooled liquid water. This ultraviscous water has a caramell-like consistency.

The metastable phase diagram shown above is tentative: it is based on the presently available data.
**Superheated water**: (p. 106): If pure water in the absence of foreign particles is heated in a smooth and homogeneous container, i.e. in the absence of condensation nuclei, then it is possible to superheat the water up to at least 110 °C without transforming it into the gaseous phase.

This is a metastable state which can eventually be dangerous, since a small mechanical shock can provoke a large gas bubble within a very short time which escapes the vessel explosively: as a result, the liquid itself can escape very rapidly, a reaction which occurs most often in narrow and large vessels.

In many cases, persons have been injured by boiling of water in the microwave heater for preparing beverages. Such water can easily be superheated and at certain conditions (i.e. by dipping a spoon into the water or by adding granular grains of coffee to it) it can provoke violent boiling or even dangerous explosions.

The colder water in the upper part of the Geysir exerts a pressure onto the underlying hot water and acts as a vessel pressure cooker. In this way the boiling water becomes superheated, i.e. it remains liquid above 100 °C.

Vapour bubbles which splash through the openings, cause a reduction of the pressure in the inner part of the Geysir. The superheated water transforms violently to vapour and seeths upwards, where it splashes as a vapour or water fountain.

**Supercooled water**: (s. pp 99, 106, 107). Water contains usually condensation nuclei (such as ice crystals, impurities or irregularities at the surface of the vessel); it freezes at 0 °C. In our normal environment, such nuclei exist almost always, such that the freezing (of still water) takes indeed place at 0 °C.

In the laboratory it was, however, possible to keep very pure and still water in the liquid state down to -70 °C by very slow cooling! Thus supercooled water is metastable: it freezes at once if condensation nuclei are added.

In the atmosphere, supercooled water is present very frequently. At temperatures between 0 and -12 °C, the concentration of supercooled water droplets is even higher than that of ice crystals but by decreasing the temperature further, the number of ice crystals continually increases. At a temperature of -20 °C the ratio of supercooled water droplets and ice crystals is 1:1. At still lower temperatures, the concentration of ice crystal becomes larger than that of supercooled water. Supercooled water droplets exist in the atmosphere down to temperatures of -40 °C (see Chapter 4: Appendix 4_A_3_1).
2.9 Colours and Spectra of Water

Colours and spectra of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$

$\text{H}_2\text{O}$: very weak absorptions in the red and yellow spectral range, but transparent in the blue region $\Rightarrow$ in large depths it appears blue!

$\text{D}_2\text{O}$: no absorption in the red and yellow range $\Rightarrow$ colourless!

Light water ($\text{H}_2\text{O}$) and light ice are the only chemical substances known until now, for which the colours are due only to molecular vibrations (overtones - and combinations of the fundamental vibrations, see pp 112 - 114)!

The colours of most other substances originate from light–induced electronic excitations [Example: red colour of copper].
Absorption of water and ice from the Far–Infrared (FIR) to the Ultraviolet (UV) spectral range

The weak absorptions in the Near Infrared (NIR) are overtones and combinations of the normal vibrations (fundamentals) in the IR and FIR. They are produced by anharmonic coupling of the fundamental vibrations!

1 THz (Terahertz) = 1 Trillion Hertz = 10^{12} Hz
The assignment of the absorption bands is illustrated at p. 114
As shown in the Figure, the absorption bands of ice are located at slightly displaced frequencies with respect to the corresponding bands of water.
In the Micro-Wave (MW): Reorientation of the permanent dipole moments of the Water molecules: “Dipolar Relaxation”

In the Infrare (IR): Molecular vibrations: (internal and external)
In the Near Infrared (NIR) to the visible region (VIS): Overtones and combinations

In the Ultraviolet (UV): Plasma absorption

Optical constants:
Refractive index \( n(\nu) \) and absorption coefficient \( \alpha(\nu) \) of liquid water

Complex dielectric constant \( \varepsilon(\nu) = \varepsilon_1(\nu) + i\varepsilon_2(\nu) \)

Dispersion and absorption of liquid water

- In the microwave range: directional changes of the permanent dipole moments of the water molecules: “Dipolar Relaxation”
- In the infrared range: molecular vibrations: (internal and external)
- In the Near Infrared (NIR) up to the Visible range (VIS): overtones and combinations

- In the UV: electronic plasma absorptions
There exist several analytical and MD models. The most popular model is the Onsager-Kirkwood-Fröhlich model which gives

\[ \varepsilon_s(T) = \varepsilon_\infty + 2 \pi N \left( \frac{m^2}{k_B T} \right) g \]

\[ \varepsilon_\infty \approx 4.2 \] contributions of molecular vibrations and electronic polarization.

N = number of molecules per unit volume.

m = permanent dipole moment of a water molecule in liquid water \((m = 3.0 \text{ Debye})\).

g = correlation factor of Kirkwood; \(g\) is a measure for the orientational correlation between a "central" molecule and his surrounding molecules \((g = 2.6 \text{ at } 0 \degree \text{C and } g = 2.46 \text{ at } 83 \degree \text{C})\).

The factor \(k_B T\) in the denominator takes into account the thermal motion of the water molecules, which counteracts the alignment of the dipole moments in the electric field.

According to Kirkwood, the high dielectric constant of water is not only due to the strong polarity of the individual water molecules (large \(m\)) but also by the correlated motion of the molecules which gives rise to a large \(g\) - factor.

(For a derivation of \(\varepsilon_s(T)\) see Ref. R.2.9.7, R.2.9.8)
The strongly inhomogeneous field $\Delta E$, which emerges from the tip of the pen, partially aligns the dipole moments of the water molecules and exerts a force onto the polar liquid causing a deflection of the jet of water. The force is proportional to $F = (\Delta E/\Delta x)$; $\Delta x$ = diameter of the jet of water; $\Delta E$ = change of $E$ across $\Delta x$. 

\[
F = \left(\frac{\Delta E}{\Delta x}\right)
\]
Here, water is subjected to a tension!

Generation of a “water bridge” by a high electric field

Centrifugal method for the generation of a very large stress (negative pressure) in water

J.M. Briggs (NBS): the water column contained in a horizontally rotating capillary tube breaks apart only at very high negative pressures; at about 10 °C the negative pressure reaches a maximum value of about -277 bar (!) and decreases by about 22% as the temperature is increased to 50 °C.

Temperature (°C)

Rupture as a result of loss of inner cohesion of the liquid and/or by the loss of adhesion at the walls of the capillary?

Between 0 °C and 10 °C, the limiting pressure undergoes an enormous increase of more than 90%! It presents another anomaly in the behavior of water in this interesting region.
„Setting to music“ the Infrared spectrum of liquid water (p. 114) by transformation into the audible acoustic range (Concerning „Water in Music“ s. Chapter 8, Section 4) (P. Brüesch, 28. 1. 2009)

Transformation of the infrared-spectrum of liquid water (s. p. 114) into the audible acoustic range:

⇒ „Setting to music“ of water
Remarks concerning the „setting to music“ of the infrared spectrum of water:

The spectrum of Figure 124 has been generated from the infrared spectrum (IR) of water shown in Figure 114 by reducing each frequency by the factor $2^{36.5}$: this corresponds to a reduction of each IR frequency by 36.5 octaves, thereby transforming it into the audible acoustic range.

The reduction factor has been chosen in such a way that the frequency of the hindered rotation at 20 THz (Figure 114) is set to the sound frequency at 220 Hz. The concert pitch a’ is fixed at 440 Hz.

The spectrum shown at p. 124 comprises more than 8 octaves each having 12 semitones; in the Figure the semitones are indicated by the small red circles. In the linear frequency scale of this spectrum, the individual semitones are distributed very densely at low frequencies, but their distances increase strongly with increasing frequency. The frequency $f_n$ and their distances are given by

$$f_n = 2^{(n/12)} f_0, \quad \Delta f_n = f_{n+1} - f_n = (2^{1/12} - 1) * f_n = 0.05946 * f_n.$$  

where $n = 0, 1, 2, \ldots, 101$, and $f_0$ has been chosen to be 4.33 Hz. For music, the 6 important octaves are:

``c - c ; c' - c ; c - c' ; c'' - c' ; c''' - c'''''' , and c''''' - c'''``

where `c = 32.7 Hz and c''' = 2092 Hz`, which corresponds approximately to the register of the piano. Some important sounds are indicated in the Figure. For a „setting to music“ it would probably be necessary to take into account the large widths of the IR-absorption bands: transformed into music, the broad and asymmetric band at 220 Hz, for example, should be decomposed into two or three bands at lower frequencies.

The designation of the sounds `c , a , cis' , els' and cis''''' refers to the Figure at p. 124.

In this representation, the distance $d$ between two neighbouring points is $d = 1/12 = 0.0833333 = constant$
Since the water molecules in ice are more strongly bound than in liquid water, the water vapour pressure over the ice is smaller than over the supercooled water. If, however, we are not considering bulk ice and bulk water but rather water droplets and snow crystals in clouds (s. Chapter 4, p. 4-A-3-1), a maximum vapor pressure difference is observed at about -15 °C but below about -50 °C the vapor pressure curves are again practically identical (Bergeron – Findeisen – Process).
References : Chapter 2

2. Physical and chemical properties

From the Figures contained in this Chapter more than one half of them have been prepared, completed and suitably arranged by the present author. If ever possible, I have cited the original literature but in other cases it was only possible to quote the corresponding Internet citation. In general, the Literature given here contains the general aspects and information of this extremely vast subject. In addition, a lot of information stems from Lectures given by the author (Reference R.2.0.1 and R.2.0.2 below).

2.0 General References

R.2.0.1 WATER: PHYSICAL PROPERTIES AND IMPLICATIONS FOR NATURE
P. Brüesch:
Lectures given in the „Troisième Cycle du Département de Physique de l’EPFL; Sémestre d’Eté (1998), and References cited therein.

R.2.0.2 POTENTIAL TECHNOLOGICAL APPLICATIONS OF WATER-BASED DIELECTRIC LIQUIDS: PHYSICAL AND CHEMICAL PROPERTIES
P. Brüesch, ABB Report, 09-00 V4 TN (3.2.2000) and References given therein.

R.2.0.3 PHYSICAL CHEMISTRY
(Phase Diagrams of Water, p. 245)

R.2.0.4 PHYSICAL CHEMISTRY
(Phase Diagrams of Water, p. 187)

R.2.0.5 PHYSIK
(Phase Diagrams of Water, p. 231)
## 2.2 Water vapour, Molecules, Hydrogen bonds and Clusters

### R.2.2.1

About the „Thermal motion of Water molecules“:
Ref. R.2.0.1; p. 19; Ref. R.2.0.2; p. 4; Ref. R.2.0.3; p. 599; Ref. R.2.0.4; p. 580.

### R.2.2.2

The infrared spectrum of water vapour (p. 38) has been measured by P. Brüesch.

### R.2.2.3

THE HYDROGEN BOND: Recent Developments in Theory and Experiments
Eds.: P. Schuster, G. Zundel, C. Sanderfof
North-Holland Publishing Company (1976)
(Hydrogen bonds in clusters and in liquid water: s. pp 39–45; 50; 55, 56; 59; 61, 62; 76; 78; 87, 88; in present Chapter)

### R.2.2.4

p. 45: HF: whatischemistry.unina.it (found under Bilder von „Hydrogen bonds in HF“)
NH₃: www.elmhurst.edu/~chem216/othermolecules.html

## 2.3 The Ices of Water

### R.2.3.1

PHYSICS OF ICE

### R.2.3.2

PHYSICS AND CHEMISTRY OF ICE
Proceedings of the International Symposium on the Physics and Chemistry of Ice, held in Sapporo, Japan, 1-6 September 1991

### R.2.3.3


### R.2.3.4

The Figure at p. 55 is contained in: ESRF Highlights 1995/96

### R.2.3.5

p. 56: Structure of Ice X: Magali Benoit, Dominik Marx and Michele Parrinello

### R.2.3.6

A comprehensive and updated list of the modifications of the ices of water is contained in Reference R.2.0.1, p. 205.

## 2.4 Liquid Water: Structure and Properties

### R.2.4.1

pp 52, 53: Snow crystals: s. also pp 176–182 and References R.4.3.6 – R.4.3.7

### R.2.4.2

Figure from p. 55 from: ESRF Highlights 1995/96; pp 55-57; References R.2.0.11 – R.2.0.13

### R.2.4.3

p. 56: Structure of Ice X: Magali Benoit, Dominik Marx and Michelle Parrinello

### R.2.4.4

A comprehensive and updated list of the Ices of Water is contained in the Reference R.2.0.1, p. 205.

## 2.5 Anomalien des Wassers

### R.2.5.1

An extensive List of the anomalies is given in Ref. R.2.0.1, Section 1.4, pp VI–IX.

### R.2.5.2


### R.2.5.3

p. 69: For other anomalies: s. Reference R.2.0.17.
2.6 Density and specific heat

R.2.6.1 p. 73: Density as a function of temperature in the range 0°C und 10°C

R.2.6.2 Density of liquid water:
Figure at p. 74 adapted and designed by P. Brüesch in Referenz R.2.0.2, p. 33

R.2.6.3 Specific heat $C_p$: Figures 76 and 77:
Figures adapted and designed by P. Brüesch in Reference R.2.0.2, p. 35

R.2.6.4 Reason and significance of the large specific heat of water:
http://www.sciencebyjones.com/specific_heat1.htm

2.7 Various physical Properties and Experiments

R.2.7.1 The Figures at pp 81 - 85 have been prepared and designed by P. Brüesch.
As far as possible, the relevant References are quoted.
see P. Brüesch: Reference R.2.0.2, pp 34 - 38

R.2.7.2 p. 85: Water has the highest surface tension of all non-metallic liquids!
http://en.wikipedia.org/wiki/Properties_of_water; see also Ref. R.2.0.2: p. 36

R.2.7.3 p. 86: Water strider walking on water due to high surface tension
see: de.academic.ru/dic.nsf/ dewiki/1491187
and: en.wikipedia.org/wiki/Gerridae

R.2.7.4 p. 89: pH(T):
Jim Clark, 2002
http://www.chemguide.co.uk/physical/acidbaseequia/kw.html

R.2.7.5 p. 91: Temperature dependence of the mobility

R.2.7.6 p. 92: Temperature dependence of ionic conductivity of pure water

R.2.7.7 p. 94: Pressure dependence of ionic conductivity of pure water:
W.A. Zisman, Phys. Rev. 29, 151 (1932); adapted by P. Brüesch in Ref. R.2.0.2, p. 42

R.2.7.8 p. 95: „The electric double layer at a metal electrode in pure water”
Peter Brüesch and Thomas Christen: J. Appl. Physics, 95, No. 5, 2004
pp. 2846 – 2856

2.8 Phase Diagrams of pure Water

R.2.8.1 pp 99 – 107: Phase diagrams of Water: the Figure at p. 92 shows superheated water (meta-
stable), both, by overheating at constant pressure as well as by reduction of pressure at constant temperature.

R.2.8.2 p. 105: Melting point and boiling point:
http://www.zeno.org/Meyers-1905/A/H%C3%B6henmessung
Mount Everest:
http://wikipedia.org/wiki/Mount_Everest

R.2.8.3 p. 106: Phase diagram of water, p. 245 in Reference R.2.0.3

R.2.8.4 p. 107: Phase diagram of water, p. 187 in Reference R.2.0.4

R-2-7

2 – 58
2.9 Colours and Spectra of Water

R.2.9.1 p. 111: Absorption of H$_2$O and D$_2$O: from [www.webexhibits.org/causesofcolor/58.html](http://www.webexhibits.org/causesofcolor/58.html)


R.2.9.3 p. 113: The spectra of ice and water have been collected from different Literatur – data by P. Brüesch.

R.2.9.4 p. 114: The infrared spectrum has been composed by P. Brüesch, using data from H.D. Downing and D. Williams (J. of Geophysical Research 80, 1656 (1975)).

R.2.9.5 p. 115: Infrared absorption spectra of liquid water and ice
Figure composed by P. Brüesch from different Literature data

R.2.9.6 p. 116: Refractive index $n(v)$ and absorption coefficient $a(v)$ of pure water:
Figure from: J.D. Jackson: Classical Electrodynamics, John Wiley & Sons, p. 291 (1975)
Explanations to the Figure from P. Brüesch:
above: Index of refraction; below: absorption coefficient a of pure water at N.T.P. conditions.
The small vertical arrows indicate the energy scale in units of $\text{eV}$ and the vertical small dashes indicate the wavelength scale. The visible range of the spectrum is illustrated by the two vertical dashed lines. Note the logarithmic scale in both direction.

R.2.9.7 p. 117: Complex dielectric constant $\varepsilon_r(v) = 1 + i\varepsilon_i(v)$ of H$_2$O as a function of frequency s. Referenz R.2.0.1

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R.2.9.8 p. 118: Static dielectric constant $\varepsilon_r(T)$
$\varepsilon_r(T)$ as a function of temperature
The explanations for the different spectral ranges have been added by P. Brüesch


2.10 Various Topics

R.2.10.1 p. 120: Dielektrophoresis

R.2.10.2 p. 121: Explanations to experimental details for „Floating Water Bridges“

R.2.10.3 p. 122: Comments to „Water under tension“

R.2.10.4 pp 123 - 126:
Transformation of the Infrared Spectrum of liquid Water into the Audio–Acoustic Frequency Range
Proposal by P. Brüesch

R.2.10.5 Saturation vapor pressure over water and ice
Appendix: 2_A_8_1 / in: Ice Properties - Caltech
[www.its.caltech.edu/~atomic/snowcrystals/ice/ice.htm](http://www.its.caltech.edu/~atomic/snowcrystals/ice/ice.htm)

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