

# Hydro Mastery



# Hydro Mastery:

*Transforming the Science of  
Water into Global Economic  
Advantage*

By

Jürgen R. Koppe and Jan Koppe

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Economic Advantage

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*Fig. 0.1: The water – powerful dynamics of the structure behind.*

“Water is the driving force in nature.”  
—Leonardo da Vinci.



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## LIST OF ABBREVIATIONS AND ACRONYMS

BB:	Broken Bonds
BET:	Brunauer–Emmett–Teller
BHB:	Broken Hydrogen Bonds
BimschVO:	Ordinance for the implementation of the Federal Immission Control Act
BW	Bulk Water
CB	Closed Bonds
CIP	Clean-in-place
DIN	German Institute for Standardization e.V.
fig	Figure
GDR	German Democratic Republic
HW	Hydration Water
IA	Icy Associates
IR Range	Infrared Range
LA	Linear Associates
mono	Monomolecular
MW	Molecular Water
NPSH	Net Positive Suction Head
ORP	Oxidation Reduction Potential
QHSE	Quality, Health, Safety & Environment
RH	Relative Humidity
SEM	Scanning Electron Microscope
Tab	Table
THM	Trihalomethanes
tot	Total
VIS Range	Visible Range
X <sub>MW</sub>	Mole Fraction of Molecular Water

# SUMMARY

Water, a seemingly mundane substance, is revealed as a critical economic actor with profound technical implications in "Water - the Substance That Looks Ordinary but Has Extraordinary Properties" (LUKSCHANDERL 1991). In this seminal work, we unlock water's secrets, translating its complex chemistry into a competitive advantage across various sectors, from agriculture to industrial manufacturing, food production, and even domestic applications.

This book does more than merely catalog water's properties; it provides a sophisticated framework for modeling water's intricate behavior. As industries aim to enhance efficiency and sustainability, understanding water at a molecular level allows for revolutionary improvements in operation. Improved models correlate with increased longevity of facilities, precision in chemical usage for treatment, and significant reductions in maintenance costs. The knowledge imparted here is not just scientific - it is a blueprint for economic efficiency.

We present a novel methodology that conceptualizes water's structure as a cyclic process, energized by external forces, that moves through dissociation and reassociation of molecules. This process is crucial for sectors where water's properties - such as viscosity, thermal conductivity, and permittivity - are central to the efficacy of operations. By applying the *ARRHENIUS* equation, the book elucidates the temperature-dependent behaviors that dictate these properties, guiding industries in process optimization.

Moreover, the interaction of water with various forms of energy, from ultrasound to UV radiation, has vast implications for improving practices in water treatment and conservation, impacting everything from large-scale desalination to the fine-tuning of home heating systems. Understanding the contraction behavior of water when dissolving substances like alkali chlorides offers insights into osmotic processes, critical for food production and water purification.

The dynamic nature of water is also explored, especially the formation of vapor bubbles in turbulent flows - a phenomenon with implications for both

the prevention of *Legionella* outbreaks in public health and the mitigation of cavitation in industrial systems. By manipulating factors such as salt concentration and introducing innovative materials, we can not only predict but also control and minimize the formation of these bubbles, leading to nanobubble technology that promises to maintain complex water systems free of fouling issues.

In the agricultural sector, this knowledge translates to more precise irrigation techniques, improved nutrient delivery systems, and enhanced understanding of crop-water interactions, leading to higher yields and reduced resource waste. In the industrial sphere, the applications extend to optimizing heating and cooling systems, improving waste treatment processes, and enhancing the quality control in manufacturing.

The concluding chapter bridges theory with practice, showcasing select technical applications backed by long-term experience. Here, we demonstrate how deep comprehension of water chemistry has been leveraged to yield substantial economic benefits, reduce environmental impacts, and enhance product and service quality across multiple industries.

This book is more than a scientific treatise; it is an indispensable tool for professionals determined to master the technical and economic challenges of water utilization in an increasingly resource-conscious world.

## ACKNOWLEDGEMENTS

This book stands as a testament to the collective effort and expertise that has been poured into the comprehensive study of water's multifaceted role in technology and economy. It is a culmination of long-term projects that span industrial and domestic realms, ranging from the expansive cooling circuits of power plants to the intricate systems governing tap water, swimming pools, and the nuanced needs of the farming sector.

We extend our deepest gratitude to the numerous contributors whose research and findings have been the backbone of the publications and patents referenced herein. Their contributions are the fabric that binds the chapters of this work. We also wish to express our sincere appreciation to our university and corporate partners, whose dedication to collaboration has fueled groundbreaking advancements and promises to drive future innovations.

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Furthermore, we are thankful to Robert Koppe for his meticulous effort in creating the graphics that visually interpret complex concepts and for his keen eye in the editorial process. His talent and attention to detail have brought a clearer understanding to the readers through visual representation.

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Everyone mentioned, along with countless others who have walked this journey with us, have not only contributed to the success of this book but have also strengthened the bridge between academic research and practical application.

# INTRODUCTION

Water is a vital resource for both human needs and the functioning of our ecosystem. The availability of high-quality freshwater has been a growing problem for centuries. In areas where rainfall is irregular or drought is expected, the usage of water supplying networks is common. Parallel the combination of filtration strategies and membrane technologies has been proven to separate high quality water and salts for millions of years. Humans just started using separation and filtration technologies to provide clean water just a few thousand years ago. Such kinds of strategies are accompanied by changes on hydrate shells, which influence the entire system combined with precipitation reactions, scaling effects and microbiological troubles (e.g. *Legionella*).

Economic aspects are the driving force to make these systems more efficient. Here the existence of different structures in water repeatedly stimulates scientific and technical reflections. Important milestones were set at the end of the 19<sup>th</sup> century, by:

- *Mr. ARRHENIUS (1887) with the dissociation theory*
- *Mr. VAN'T HOFF (1887) with the derivation of the osmotic pressure*
- *Mr. REYNOLDS (1883) with the fluidic investigations*

to name just a few. These decisive advances were based on exact observations and scientific and technical principles. As a result, they had found permanent support in the professional world and formed the basis for many useful developments.

“The constitution of liquid water” by Mr. RÖNTGEN (1892) is of scientific historical value. This work marks the beginning of a series of structural investigations on water, which focused in particular on hydrogen bonds and the formation of clusters. The work by Mr. GIEGER and Mr. WIRTZ (1950) summarizes the knowledge gained up to this point in time. The decisive deficiency of this and the following considerations - the work of Mr. LUDWIG (2005) from this millennium should be mentioned here - are that these structures are viewed exclusively as "fluctuating quantities". Those are only possible if the fluctuations take place without changing the entropy, such as the reversible proton migration within the hydrogen bond.

With the description of structures and their temperature-dependent occurrence, the team around Mr. CHAPLIN (2001 & 2006) is working on water structures, which he calls LOW DENSITY WATER and HIGH DENSITY WATER. Mr. MARÉCHAL (2011) also differentiates - like CHAPLIN - between LOW DENSITY and HIGH DENSITY WATER. However the concept of the cycle with irreversible structural changes is left out both of them. The team around Mr. GALLO (2016) defines different structures in the water, considering the current state of knowledge.

At this point the concept of circularity introduced by Mr. CLAUSIUS (1891) in the 19<sup>th</sup> century with a series of irreversible reactions instead of “fluctuating transitions” is missing. With this book the idea of Mr. CLAUSIUS is taken up and combined with the current knowledge. Afterwards there is the cycle of water structures found as the result of structural elements within water. This methodology allowed modelling the temperature dependency of various water properties in a simple way.

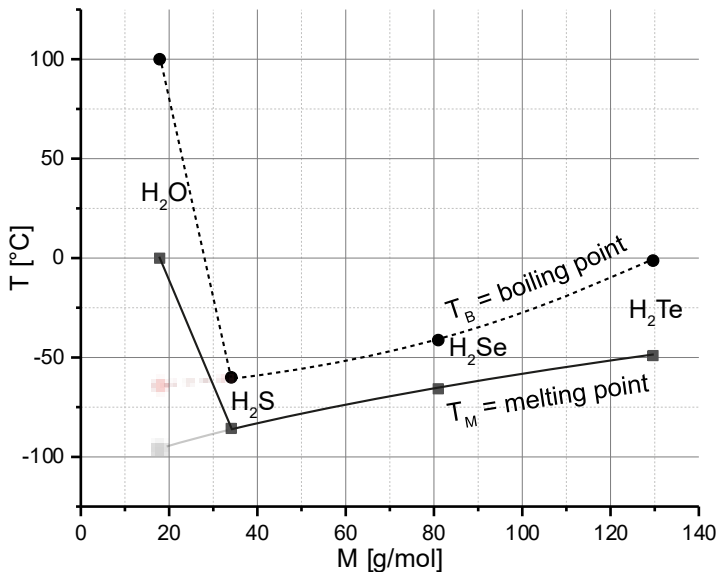
These model considerations were also used to explain the effects that can be observed when water is exposed to external energy radiation. Some interactions of water with salt solutions are also considered within this book. Another part turns to the explanation of flow processes and the sometimes puzzling occurrence of Legionella troubles. Finally, some practical applications are explained in which economic advantages were achieved by catalytic acceleration of the respective rate-determining step.

This book should be understood as an invitation to approach the water from a quite smart perspective.

# 1 THE ELEMENTAL COMPOSITION OF WATER

## 1.1 Ice, Water and Air

The elemental composition of the water is  $\text{H}_2\text{O}$ . In terms of the formula, it is comparable to the  $\text{H}_2\text{S}$ . Starting from the  $\text{H}_2\text{S}$  with a molecular weight that is almost twice as high (34 g/mol compared to 18 g/mol for water), which already boils at **minus 60 °C**, the water should boil slightly below **minus 60 °C**.



*Fig. 1.1 Theoretical and real melting and boiling point of water (based on Scheffler (1981) & Wagner (2007))*

At temperatures below  $-60^\circ\text{C}$ , it exists in its gaseous form, ready to evaporate. Transitioning between states - from solid ice influenced by entropy and enthalpy, to the liquid form we utilize daily between  $0^\circ\text{C}$  and  $100^\circ\text{C}$  - its behavior is in a study balance. Understanding this balance is paramount, as disturbances can lead to substantial energy releases, manifested in powerful natural events like massive waves and tornadoes.

For those delving deeper, around  $-60^{\circ}\text{C}$ , we can technically quantify a distinctive water vapor saturation pressure, termed  $p_{\text{H-O-H}}$ . Grasping these fundamentals not only enhances our scientific knowledge but also offers practical insights beneficial to industries, environmental studies, and our daily life.

*Tab. 1.1 Water vapor saturation pressure  $p_{\text{H-O-H}}$  in ice and water  
(Scheffler 198 & Wagner 2007)*

T [°C]	$p_{\text{H-O-H}}$ (ice) [Pa]	$p_{\text{H-O-H}}$ (water) [Pa]
0	611	611
- 1	563	568
- 2	518	528
- 3	476	490
- 4	437	455
- 5	402	422
- 10	260	287
- 20	103	126
- 30	38	51
- 40	12.8	19
- 50	3.92	6.44
- 60	1.08	1.95
- 70	0.26	0.52
- 80	0.05	0.11
- 90	0.0096	0.020
- 100	0.0013	0.0036

In the realm of supercooled temperatures below  $-100^{\circ}\text{C}$ , conventional icy structures challenge thermodynamic norms. As articulated by Mr. AMANN-WINKEL (2013), on Earth there is only one crystalline form of ice in nature. The atoms are arranged in a strictly regular structure consisting of hexagons. Under extreme conditions, especially at very low temperatures, amorphous ice is formed, which is more like liquid water, i.e. without a basic crystalline structure - it is essentially a solidified form of flowing water. In space, ice occurs almost exclusively in this amorphous form. But what's transpiring around the  $-60^{\circ}\text{C}$  mark?

Delving into the thermodynamics, the available internal energy,  $U$ , as cited by Stierstadt (2010), is:

$$U = \frac{f}{2} \cdot n \cdot R \cdot T \quad (1.1)$$

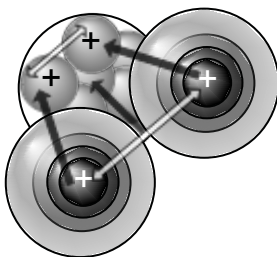


$f$  is the number of degrees of freedom (3 for ideal gases at constant pressure),  $n$  is the number of molecules, and  $R$  the ideal gas constant (valued at  $8.314 \text{ J}/(\text{mol} \cdot \text{K})$ ).

At minus  $60^\circ \text{C}$ ,  $U = 2.6 \text{ kJ/mol}$  and at  $0^\circ \text{C}$   $U = 3.3 \text{ kJ/mol}$ .

This energy is available to the water molecules to orient themselves structurally so that complete evaporation (as with  $\text{H}_2\text{S}$ ) can be avoided. The target is the minimization of entropy! Compare this value with the “activation energy of surface tension (binding of water dipoles) or the activation energy of permittivity (hydrogen bond cluster).

The water benefits from the fact that the oxygen is hybridized  $\text{sp}^3$ . I.e. oxygen has two orbitals filled with (partially positively charged) hydrogen and two free (partially negatively charged) orbitals.

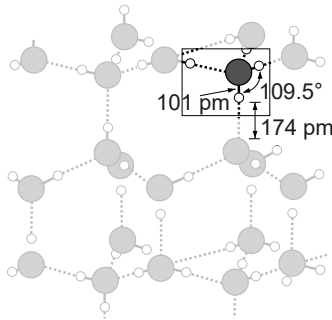


*Fig. 1.2: The water molecule (based on Schlich 2016)*

The figure shows oxygen in the **back side** and hydrogen in the **front side**

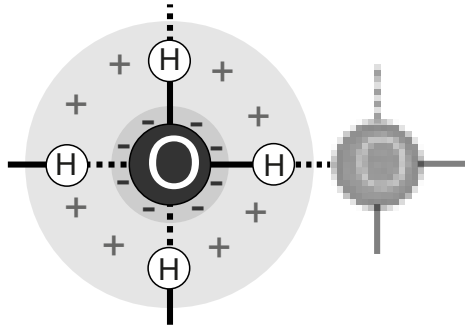
In ice structures, hydrogen bonds form with an O-O distance of only 276 pm (ref. fig. 1.6). This means that one hydrogen orbital can temporarily overlap with two oxygen orbitals of neighboring water molecules in the middle position when moving between the oxygen atoms, in the sense of a covalent bond.

This covalent part of the bond play an integral role to the melting enthalpy of ice ( $6 \text{ kJ/mol}$ ). It should be noted that the H-O-H bond angle in ice precisely mirrors that of a tetrahedron at  $109.5^\circ$  (Heise 2002).



*Fig. 1.3: H-O-H bond angle in ice (based on Lingenhöhl 2016)*

Oxygen is  $sp^3$ -hybridized in the ice with 4 degenerate - i.e. equivalent - hydrogen bonds. Between the repelling oxygen species, which are equally negatively charged, there is a tetrahedral arrangement of a positively charged space cloud formed by the hydrogen species.



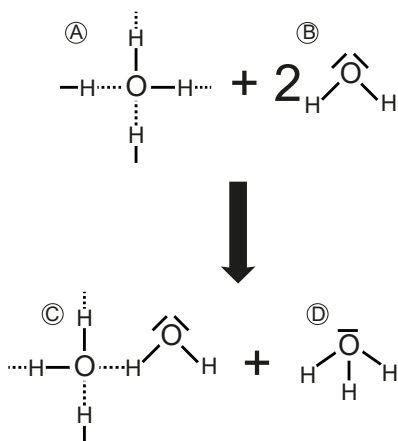
*Fig. 1.4: Structure of charged space cloud in ice*

Shielding is particularly favorable at tetrahedral sites. As a result, the O-O bond distance in ice is relatively small at 276 pm. However, the positively charged hydrogen space cloud creates a very voluminous grid due to electrostatic repulsion. This may serve as an explanation for the relatively low density of the ice structure.

Only on the ice surface is this degeneration no longer present. The positively charged space cloud is disturbed. Occasionally HO groups protrude into the room, which can dissociate and release protons. Molecular water then forms

in connection with hydroxide anions. This can either evaporate or - in conjunction with protons - react to hydrate water, which then can be further integrated in the bulk water.

The bulk water is formed and the molecular water attaches to the vacancies in the tetrahedron lattice that were left by the hydrogen. However, there is no longer a continuous, positively charged space cloud. A negative residual charge ( $\text{HO}^-$ ) remains.



*Fig. 1.5: Dissolution of ice by molecular water*

Contrasting ice, bulk water's O-O distance expands to 298 pm due to unshielded negative charge centers on the oxygen species, which corresponds to a volume increase of 25 %.

Means: 1 out of 4 protons is missing and the volume of space between the oxygen species increases by  $\frac{1}{4}$ . This "free" space is filled with molecular water. The positively charged hydrogen space charge also weakens.

Due to the decreasing hydrogen repulsion forces, the structure of water becomes more compact overall. For this reason, the density of the system increases during the transition from ice to water.

At the same time, due to the now partially unoccupied  $\text{sp}^3$  orbitals of oxygen, the bond angle of the H-O-H bond changes from  $109.5^\circ$  to  $104.5^\circ$ . In this structure, the hydrogen orbitals temporarily no longer overlap with two neighboring oxygen orbitals. That's a "pure" hydrogen bond.

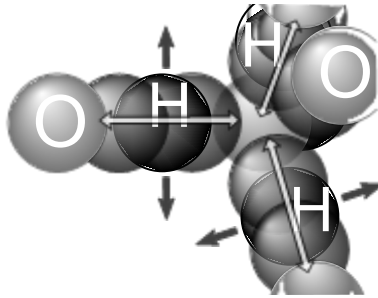
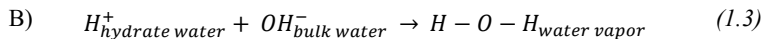
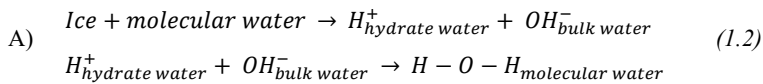


Fig. 1.6: hydrogen bond in bulk water (based on Schlich 2016)

When the molecular water is lost, the bulk water turns into ice. Consequently, an extremely thin layer of water can be found on the surface of the ice. This observation had already been made by Mr. FARADAY around the year 1850. At the time, most people just didn't believe him. Current studies validated that at minus 0.7 °C there is a 70 nm thick layer of liquid water present on the ice. This layer decreases in even colder temperatures down to minus 33 °C and then disappears completely – probably at a little below minus 60 °C (Lingenhöl 2016).

The following reaction processes are found:



\* Strictly speaking, as shown in fig. 1.5, it is not  $\text{OH}^-$ , but bulk water with excess hydroxide groups.

The whole reaction process depends on the ice surface. This means that an increase in the ice surface accelerates these processes. Reaction a) proceeds under increase of entropy (melt entropy) and an increase of enthalpy (melt enthalpy). Parallel reaction b) proceeds under decrease of entropy (water vapor entropy minus sublimation entropy) and a decrease of enthalpy (evaporation heat water vapor minus sublimation heat). That means in both cases the free reaction enthalpy is negative. Since reaction b) is proceeds faster, system's net free reaction enthalpy is negative.

As long as reaction b) (i.e. the evaporation rate of the molecular water [from the bulk water]) is faster than reaction a) (i.e. the rate of formation due to the

dissociation of the ice), the ice structure will remain stable. Thus, it is the partial release of water vapor that, in conjunction with the hydrogen bonds, stabilizes the ice system.

At normal pressure, this is also the case up to 0 °C. At 0 °C the balanced free reaction enthalpy of the system becomes zero. Beyond this point, with increasing pressure, the evaporation rate drops, leading to a higher molecular water content in the ice and consequently, melting even below 0 °C.

Adding salt also reduces the rate of evaporation of molecular water due to an increase in hydrate water formation. Therefore ice begins to melt even below 0 °C. The deliquescent moisture can be used as a measure of hydrated water formation. This moisture describes the extent to which the water vapor saturation partial pressure is reduced by the dissolved salt.

When sodium chloride solution (36 g NaCl /100 ml) is added, this pressure decreases to 75 % and when magnesium chloride (55 g  $\text{MgCl}_2 \times 6 \text{ H}_2\text{O}$  /100 ml) is added to 33 % of the water vapor saturation partial pressure (Hudy 2020).

This means that the thawing effect is significantly increased even at low temperatures, especially by adding magnesium chloride. This strategy was used in former year e.g. in the GDR (German Democratic Republic) during the 1960s and 1970s for preventing icy roads. The partial saturation pressure of water vapor below 0 °C is close to ice (ref. Tab. 1.1). The difference is due to the fact that the interaction of the bulk water with the ice structure causes the molecular water to be bound somewhat more tightly than in “free” bulk water.

## 1.2 Water & Air

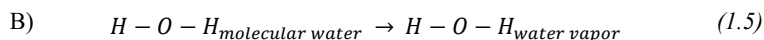
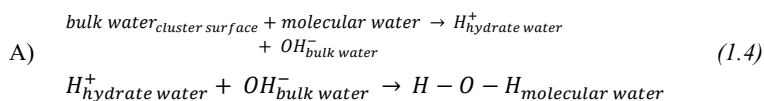
In the previous chapter was shown that the water system manifests itself through the icy structure clearly above the molar mass-related boiling point of minus 80 °C. The target is achieving the minimum of entropy. The trick is that this ice system is able to build a structure that releases a partial portion into the environment in the form of enthalpy- and entropy-rich molecular water (water vapor) through a cycle of various structures. It is important for the functioning that this release occurs faster than the formation of the molecular water. Under normal pressure this point is exceeded at 0 °C.

The water system changes to the "liquid water" state at 0 °C, combined with the following "advantages":

While only the surface structures of the ice are involved in the cycle, there is a significantly larger proportion of the system in the ice. This larger proportion is now available for the cycle via the bulk water present in clusters. Since the cluster size decreases with increasing temperature, this proportion increases continuously. As a result, the dissociation - expressed by the "dissociation constant" - increases.

The rate of evaporation of the water - expressed by the "water vapor saturation partial pressure" - increases significantly, since the molecular water is no longer prevented from evaporating by the ice structure.

The following reaction chains were found:



\* Strictly speaking, as shown in fig. 1.5, it is not OH<sup>-</sup>, but bulk water with excess hydroxide groups.

Reaction b) can proceed much faster in liquid water than in ice.

Again, the whole reaction process depends on the cluster surface, i.e. on the cluster size, which depends on the temperature, as the following paragraph shows:

“According to the cluster models by Mr. HASTED (1952), Mr. NEMETHY and Mr. SCHERAGA (1962), the liquid water consists of four-fold tetrahedral linked molecules (bulk water) and practically freely rotating single molecules (molecular water), which fill in the spaces between the clusters. The size of the clusters is around 100 molecules at 0 °C or around 25 at 70 °C; at even higher temperatures, the model no longer physically makes sense. The clusters are in constant disintegration and rebuilding.” (Atom 1970)

With decreasing cluster size, reaction a) proceeds faster and faster, until then - under normal pressure - at 100 °C reactions a) and b) proceed at the same speed, and the system “liquid water” changes into the system “water vapor”.

If you follow these model ideas, then there must be a connection between the dissociation (i.e. the dissociation constant of the water) and the water vapor saturation partial pressure.