

# Fundamental Characteristics of Water

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Title page as requested by the editor Dr. Wai-kit Nip

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## **I. Introduction**

Water, a natural occurring and abundant substance that exists in solid, liquid, and gas forms on the planet Earth, has attracted the attention of artists, engineers, poets, writers, philosophers, environmentalists, scientists, and politicians. Every aspect of life involves water as food, as a medium in which to live, or as the essential ingredient of life. The food-science aspects of water range from agriculture, aquaculture, biology, biochemistry, cookery, microbiology, nutrition, photosynthesis, power generation, to zoology. Even in the narrow sense of food technology, water is intimately involved in the production, washing, preparation, manufacture, cooling, drying, and hydration of food. Water is eaten, absorbed, transported, and utilized by cells. Facts and data about water are abundant and diverse. This article can only selectively present some fundamental characteristics of water molecules and their collective properties for readers when they ponder food science at the molecular level.

The physics and chemistry of water is the backbone of engineering and sciences. The basic data for the properties of pure water, which are found in the CRC Handbook of Chemistry and Physics (1), are useful for food scientists. However, water is a universal solvent, and natural waters contain dissolved substances present in the environment. All solutes in the dilute solutions modify the water properties. Lang's Handbook of Chemistry (2) gives solubilities of various gases and salts in water. Water usage in the food processing industry is briefly described in the Nalco Water Handbook (3). For water supplies and treatments, the Civil Engineering Handbook (4) provides practical guides. The Handbook of Drinking Water Quality (5) sets guidelines for waters used in food services and technologies. Wastewater from the food industry needs treatment, and the technology is usually dealt with in industrial chemistry (6). Most fresh food contains large amounts of water. Modifying the water content of foodstuffs to extend storage life and enhance quality is an important and widely used process (7).

A very broad view and deep insight on water can be found in "Water – A Matrix of Life" (8). Research leading to our present-day understanding of water has been reviewed in the series "Water – A Comprehensive Treatise" (9). The interaction of water with proteins (10, 11) is a topic in life science and food science. Water is the elixir of life and H<sub>2</sub>O is a biomolecule.

## **II. Water and Food Technology**

Water is an essential component of food (12). Philosophical conjectures abound as to how Earth evolved to provide the mantle, crust, atmosphere, hydrosphere, and life. Debates continue, but some scientists believe that primitive forms of life began to form in water (13). Complicated life forms developed, and their numbers grew. Evolution produced anaerobic, aerobic and photosynthetic organisms. The existence of abundant life forms enabled parasites to appear and utilize plants and other organisms. From water all life began (14). Homo sapiens are integral parts of the environment, and constant exchange of water unites our internal space with the external.

The proper amount of water is also the key for sustaining and maintaining a healthy life. Water transports nutrients and metabolic products throughout the body to balance cell contents and requirements. Water maintains biological activities of proteins, nucleotides, and carbohydrates, and participates in hydrolyses, condensations, and chemical reactions that are vital for life (15). On average, an adult consumes 2 to 3 L of water: 1-2 L as fluid, 1 L ingested with food, and 0.3 L from metabolism. Water is excreted via the kidney, skin, lung, and anus (16). The amount of water passing through us in our lifetimes is staggering.

Aside from minute amounts of minerals, food consists of plant and animal parts. Water is required for cultivating, processing, manufacturing, washing, cooking and digesting food. During or after eating, a drink, which consists of mostly water, is a must to hydrate or digest the food. Furthermore, water is required in the metabolic process.

Cells and living organisms require, contain and maintain a balance of water. An imbalance of water due to freezing, dehydration, exercise, overheating, etc. leads to the death of cells and eventually the whole body. Dehydration kills far more quickly than starvation. In the human body, water provides a medium for the transportation, digestion and metabolism of food in addition to many other physiological functions such as body temperature regulation (17).

Two-thirds of the body mass is water, and in most soft tissues, the contents can be as high as 99% (16). Water molecules interact with biomolecules intimately (9); it is part of us. Functions of water and biomolecules collectively manifest life. Water is also required for running households, making industrial goods, and generating electric power.

Water has shaped the landscape of Earth for trillions of years, and it covers 70% of the Earth's surface. Yet, for food production and technology it is a precious commodity. Problems with water supply can lead to disaster (5). Few brave souls accept the challenge to stay in areas with little rainfall. Yet, rainfall can be a blessing or a curse depending on the timing and amount. Praying for timely and bounty rainfall used to be performed by emperors and politicians, but water for food challenges scientists and engineers today.

### **III. Water Molecules and Their Microscopic Properties**

Plato hypothesized four *primal substances*: water, fire, earth, and air. His doctrine suggested that a combination and permutation of various amounts of these four *primal substances* produced all the materials of the world. Scholars followed this doctrine for 2000 years, until it could not explain experimental results. The search of fundamental substances led to the discovery of hydrogen, oxygen, nitrogen, etc., as chemical elements. Water is made up of hydrogen (H) and oxygen (O). Chemists use H<sub>2</sub>O as the universal symbol for water. The molecular formula, H<sub>2</sub>O, implies that a water molecule consists of two H atoms and one O atom. However, many people are confused with its other chemical names such as hydrogen oxide, dihydrogen oxide, dihydrogen monoxide, etc.

## A. Isotopic Composition of Water

The discoveries of electrons, radioactivity, protons, and neutrons implied the existence of isotopes. Natural isotopes for all elements have been identified. Three isotopes of hydrogen are protium ( $^1\text{H}$ ), deuterium (D,  $^2\text{D}$  or  $^2\text{H}$ ), and radioactive tritium (T,  $^3\text{T}$  or  $^3\text{H}$ ), and the three stable oxygen isotopes are  $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$ . The masses and abundances of these isotopes are given in Table 1. For radioactive isotopes, the half-lives are given.

<b>Table 1. Isotopes of hydrogen and oxygen; and isotopic water molecules</b>					
molar mass (amu), relative abundance (%) or half life					
<b>Isotopes of hydrogen</b>			<b>Stable isotopes of oxygen</b>		
$^1\text{H}$	$^2\text{D}$	$^3\text{T}$	$^{16}\text{O}$	$^{17}\text{O}$	$^{18}\text{O}$
1.007825	2.00141018	3.0160493	15.9949146	16.9991315	17.9991604
99.985%	0.015%	12.33 years	99.762%	0.038%	0.200%
<b>Isotopic water molecules</b>					
molar mass (amu) and relative abundance (% , ppm or trace)					
$\text{H}_2^{16}\text{O}$	$\text{H}_2^{18}\text{O}$	$\text{H}_2^{17}\text{O}$	$\text{HD}^{16}\text{O}$	$\text{D}_2^{16}\text{O}$	$\text{HT}^{16}\text{O}$
18.010564	20.014810	19.014781	19.00415	19.997737	20.018789
99.78%	0.20%	0.03%	0.0149%	0.022 ppm	trace

Random combination of these isotopes gives rise to the various isotopic water molecules, the most abundant one being  $^1\text{H}_2^{16}\text{O}$  (99.78%, its mass is 18.010564 atomic mass units (amu)). Water molecules with molecular masses about 19 and 20 are present at some fractions of a percent. Although  $\text{HD}^{16}\text{O}$  (0.0149%) is much more abundant than  $\text{D}_2^{16}\text{O}$  (heavy water, 0.022 part per million),  $\text{D}_2\text{O}$  can be concentrated and extracted from water. In the extraction process,  $\text{HDO}$  molecules are converted to  $\text{D}_2\text{O}$  due to isotopic exchange. Rather pure heavy water ( $\text{D}_2\text{O}$ ) is produced on an industrial scale especially for its application in nuclear technology, which provides energy for the food industry.

A typical mass spectrum for water shows only mass-over-charge ratio of 18 and 17 respectively for  $\text{H}_2\text{O}^+$  and  $\text{OH}^+$  ions in the gas phase. Other species are too weak for detection, partly due to condensation of water in mass spectrometers.

The isotopic composition of water depends on its source and age. Its study is linked to other sciences (18). For the isotopic analysis of hydrogen in water, the hydrogen is reduced to a hydrogen gas and then the mass spectrum of the gas is analyzed. For isotopes of oxygen, usually the oxygen in  $\text{H}_2\text{O}$  is allowed to exchange with  $\text{CO}_2$ , and then the isotopes of the  $\text{CO}_2$  are analyzed. These analyses are performed on archeological food remains and unusual food samples in order to learn their origin, age, and history.

## B. Structure and Bonding of Water Molecules

Chemical bonding is a force that binds atoms into a molecule. Thus, chemists use H-O-H or HOH to represent the bonding in water. Furthermore, spectroscopic studies revealed the H-O-H bond angle to be  $104.5^\circ$  and the H-O bond length to be 96 picometers (pm) for gas H<sub>2</sub>O molecules (19). For solid and liquid, the values depend on the temperature and states of water. The bond length and bond angles are fundamental properties of a molecule. However, due to the vibration and rotational motions of the molecule, the measured values are average or equilibrium bond lengths and angles.

The mean van der Waals diameter of water has been reported as nearly identical with that of isoelectronic neon (282 pm). Some imaginative models of the water molecule are shown in Fig. 1

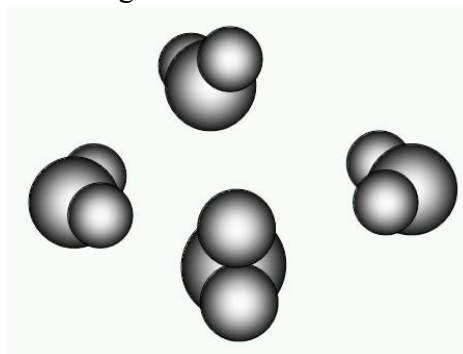


Fig. 1. Some imaginative models of water molecules

An isolated water molecule is hardly static. It constantly undergoes a vibration motion that can be a combination of any or all of the three principle modes: symmetric stretching, asymmetric stretching, and bending (or deformation). These vibration modes are indicated in Fig. 2.

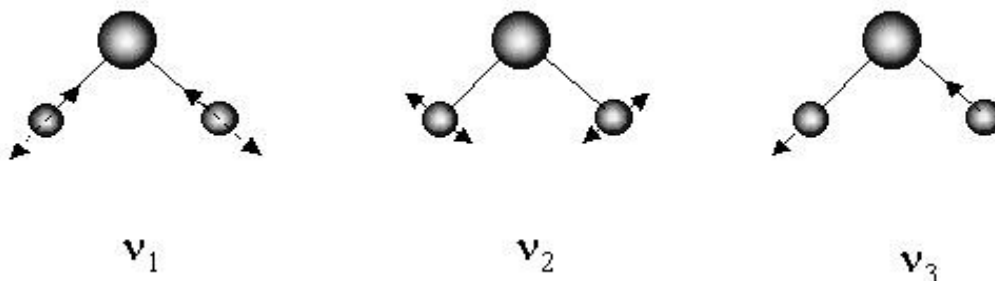


Fig. 2. The three principle vibration modes of the water molecule, H<sub>2</sub>O:  $n_1$ , symmetric stretching,  $n_2$ , bending, and  $n_3$ , asymmetric stretching.

Absorption of light (photons) excites water molecules to higher energy levels. Absorption of photons in the infrared (IR) region excites the vibration motion. Photons exciting the symmetric stretching, bending, and asymmetric stretching to the next higher energy levels have wave numbers 3656, 1594, and 3756  $\text{cm}^{-1}$  respectively, for H<sub>2</sub>O (20). These values and those for other water molecules involving only <sup>16</sup>O are given in Table 2

**Table 2. Absorption frequencies of D<sub>2</sub>O, H<sub>2</sub>O, and HDO molecules for the excitation of fundamental modes to a higher energy level.**

Vibration mode	Absorption energies in wave numbers (cm <sup>-1</sup> )		
	H <sub>2</sub> O	HDO	D <sub>2</sub> O
Symmetric stretching	3656	2726	2671
Bending	1594	1420	1178
Asymmetric stretching	3756	3703	2788

The spectrum of water depends on temperature and density of the gaseous H<sub>2</sub>O. A typical IR spectrum for the excitation of only the fundamental vibration modes consists of three peaks around 1594, 3656 and 3756 cm<sup>-1</sup>. Additional peaks due to excitation to mixed modes appear at higher wave numbers.

Rotating the H<sub>2</sub>O molecule around the line bisecting the HOH angle by 180° (360°/2) results in the same figure. Thus, the molecules have a 2-fold rotation axis. There are two mirror planes of symmetry as well. The 2-fold rotation and mirror planes give the water molecules the symmetry point group C<sub>2v</sub>.

Rutherford alpha scattering experiment in 1909 showed that almost all atomic mass is in a very small atomic nucleus. In a neutral atom the number of protons in the nucleus is the same as the number of electrons around the nucleus. A proton and an electron have the same amount, but different kind of charge. Electrons occupy nearly all of the atomic volume, because the radius of an atom is 100,000 times that of the nucleus.

Electrons, in quantum mechanical view, are waves confined in atoms, and they exist in several energy states called orbitals. Electrons in atoms and molecules do not have fixed locations or orbits. Electron states in an element are called electronic configurations, and their designation for H and O are 1s<sup>1</sup>, and 1s<sup>2</sup>2s<sup>2</sup>2p<sup>4</sup>, respectively. The superscripts indicate the number of electrons in the orbitals 1s, 2s or 2p. The electronic configuration for the inert helium (He) is 1s<sup>2</sup>, and 1s<sup>2</sup> is a stable core of electrons. Bonding or valence electrons are 1s<sup>1</sup> and 2s<sup>2</sup>2p<sup>4</sup> for H and O respectively.

The valence bond approach blends one 2s and three 2p orbitals into four bonding orbitals, two of which accommodate two electron pairs. The other two orbitals have only one electron each, and they accommodate electrons of the H atoms bonded to O, thus forming the two H–O bonds. An electron pair around each H atom and four electron pairs around the O atom contribute stable electronic configurations for H and O, respectively. The Lewis dot-structure, Fig. 3, represents this simple view. The two bonding and two lone pairs are asymmetrically distributed with major portions pointing to the vertices of a slightly distorted tetrahedron in 3-

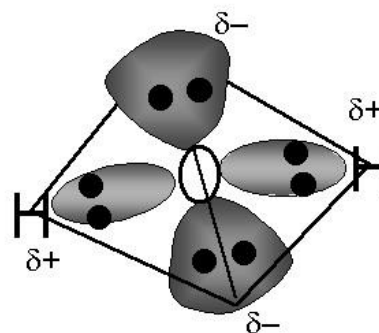


Fig. 3. A tetrahedral arrangement of the Lewis dot-structure and charge distribution of the H<sub>2</sub>O molecule.

dimensional space. The two lone pairs mark slightly negative sites and the two H atoms are slightly positive. This charge distribution around a water molecule is very important in terms of its microscopic and macroscopic, chemical and physical properties described later. Of course, the study of water continues and so does the evolution of bonding theories. Moreover, the distribution of electrons in a single water molecule is different from those of dimers, clusters, and bulk water.

The asymmetric distribution of H atoms and electrons around the O atom results in positive and negative sites in the water molecule. Thus, water consists of polar molecules.

The **dipole moment**,  $\mu$ , is a measure of polarity and a useful concept. A pair of opposite charge,  $q$ , separated by a distance,  $d$ , has a dipole moment of  $\mu = d q$  with the direction pointing towards the positive charge as shown in Fig. 4.

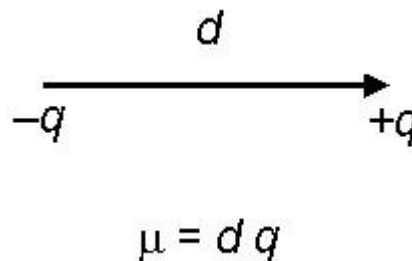


Fig. 4. Separation of a positive and a negative charge  $q$  at a distance  $d$  results in a dipole,  $\mu = d q$

The dipole moment of individual water molecules is  $6.187 \times 10^{-30}$  C m (or 1.855 D) (21). This quantity is the vector resultant of two dipole moments due to the O–H bonds. The bond angle H–O–H of water is  $104.5^\circ$ . Thus, the dipole moment of an O–H bond is  $5.053 \times 10^{-30}$  C m. The bond length between H and O is 0.10 nm, and the partial charge at the O and the H is therefore  $q = 5.053 \times 10^{-20}$  C, 32 % of the charge of an electron ( $1.6022 \times 10^{-19}$  C). Of course, the dipole moment may also be considered as separation of the electron and positive charge by a distance 0.031 nm.

It should be pointed out that the dipole moments of liquid and solid water appear to be higher due to the influence of neighboring molecules. For the liquid and solid, macroscopic properties need be considered.

### C. Hydrogen Bonds

Attraction among water molecules is more than polar-polar in nature. The O atoms are small and very electronegative. As a result, the positive H atoms (protons) are very attractive to the negative O atoms of neighboring molecules. This O - - H - O strong attraction is called a **hydrogen bond**, a concept popularized by L. Pauling (22). Furthermore, hydrogen atoms bonded to atoms of N and F, neighboring elements of O in the periodic table, are positive, and they form hydrogen bonds with atoms of N, O, or F. The strength of hydrogen bonds depends on the X–H - -

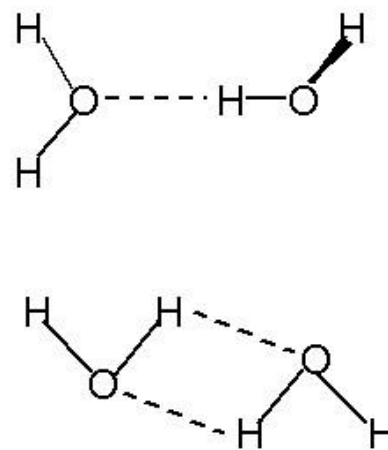


Fig. 5. Two possible structures of the water dimer,  $(\text{H}_2\text{O})_2$



- Y (X or Y are N, O, or F atoms) distances and angles; the shorter the distances, the stronger are the hydrogen bonds.

When two isolated water molecules approach each other, a dimer is formed due to hydrogen bonding. The dimer may have one or two hydrogen bonds. Dimers exist in gaseous and liquid water. When more water molecules are in close proximity, they form trimmers, tetramers and clusters. Hydrogen bonds are not static, they exchange protons and partners constantly. Hydrogen bonding is a prominent feature in the structures of various solid phases of water usually called ice as we shall see later.

Water molecules not only form hydrogen bonds among themselves, they form hydrogen bonds with any molecule that contains N-H, O-H and F-H bonds. Foodstuffs such as starch, cellulose, sugars proteins, DNA, and alkaloids contain N-H and O-H groups, and these are both H-donors and H-acceptors of hydrogen bonds of the type N- - H-O, O- -H-N, N- -H-N, etc. A dimer depicting the hydrogen bond and the van der Waal sphere of two molecules is shown in Fig. 6 (23).

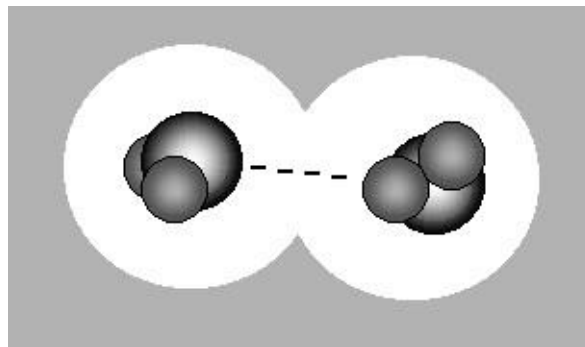


Fig. 6. Hydrogen-bond and the van der Waal sphere of two water molecules, by permission from M.F. Martin (23), [sbu.ac.uk/water/molecule.html](http://sbu.ac.uk/water/molecule.html)

Carbohydrates (starch, cellulose and sugars) contain H-C-O-H groups. The O-H groups are similar to those of water molecules, and they are H-acceptors and H-donors for hydrogen bonds. Proteins contain O-H, R-NH<sub>2</sub> or R<sub>2</sub>>NH groups, and the O-H and N-H groups are both H-donors and H-acceptors for the formation of hydrogen bonds. Thus, water molecules have intimate interactions with carbohydrates and proteins.

#### IV. Macroscopic Properties of Water

Collectively, water molecules exist as gas liquid, or solid depending on the temperature and pressure. These phases of water exhibit collective or macroscopic properties such as phase transitions, crystal structures, liquid structures,

**Table 3. Thermodynamic constants for phase transitions of H<sub>2</sub>O (molar mass, 18.015268 g mol<sup>-1</sup>) at 101.314 kPa pressure.**

	Fusion (melting)	Boiling	Vaporization Sublimation
<b>Temperature K</b>	273.15	373.15	273.16
$\Delta H$ kJ mol <sup>-1</sup>	6.01	40.66	51.06
$\Delta S$ J mol <sup>-1</sup> K <sup>-1</sup>	22.00	108.95	186.92
$\Delta E$ kJ mol <sup>-1</sup>	6.01	37.61	48.97
$\Delta V$ L mol <sup>-1</sup>	-1.621	30.10	-

Energy change of phase transition:  $\Delta H$ , enthalpy;  $\Delta S$ , entropy;  $\Delta E$ , internal energy.  $\Delta V$ : volume change of phase transition.

vapor pressures, and volume-pressure relationships of vapor. In addition, energies or enthalpies for melting, vaporization and heating are also important for applications in food technology.

Thermodynamic constants for phase transitions given in Table 3 are those of pure water. Natural waters, of course, contain dissolved air, carbon dioxide, organic substances, microorganisms, and minerals. Water in food or used during food processing usually contains various organic and inorganic substances. These solutes modify the properties of water and caution should be taken to ensure proper values are applied in food technology.

The triple point and boiling points of water are defined as 273.16 and 373.16 K (kelvin) in the SI unit of temperature, respectively. Thus, the temperature differences can be in units of K or °C.

Water has many unusual properties due to its ability to form hydrogen bonds and its large dipole moment. As a result, the melting, boiling and critical points for water are very high compared to substances of similar molar masses. In general, the higher the molar masses, the higher are the melting and boiling points of the material. Associated with these properties are its very large heat of melting, heat capacity, heat of vaporization and heat of sublimation. Moreover, its surface tension and viscosity are also very large. Thermodynamic energies, and volume changes for phase transitions of H<sub>2</sub>O are summarized in Table 3. These data are mostly taken from the Encyclopedia of Chemical Technology, Vol. 25 (1991) (24).

### A. Crystal Structures and Properties of Ice

Hydrogen bonding is prominent in the crystal structures of various solid phases of H<sub>2</sub>O. The triple point of water is at 273.16 K and 4.58 torr (611 Pa). The melting point at 1.00 atm (760 torr or 101.325 kPa) is used to define the Kelvin scale as 273.15 K. When water freezes at these temperatures and atmospheric pressure or lower, the solids are hexagonal ice crystals usually designated as I<sub>h</sub>.

Properties of I<sub>h</sub> are given in Table 4. Snowflakes have many shapes because their growth habit depends on temperature and vapor pressure, but they all exhibit hexagonal symmetry, due to the hexagonal structure of ice (25).

**Table 4. Properties of Ice at 273.15 K**

Heat of formation $\Delta H_f$	292.72 kJ mol <sup>-1</sup>
Density	0.9168 g cm <sup>-3</sup>
Heat capacity	2.06 J g <sup>-1</sup> K <sup>-1</sup>
$\Delta H_{\text{fusion}}$	6.01 kJ mol <sup>-1</sup>
Dielectric constant at 3 kHz	79
Thermal expansion coefficient	
Volumetric	$120 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1} \text{ K}^{-1}$
Linear	$52.7 \times 10^{-6} \text{ cm g}^{-1} \text{ K}^{-1}$

However, from a geometric point of view, the same bonding may also be arranged to have cubic symmetry. The existence of cubic ice has been confirmed. When water vapor deposits onto a very cold, 130 – 150 K, surface or when small droplets are cold under low

pressure at high altitude, the ice has a cubic symmetry usually designated as  $I_c$ . At still higher pressures, different crystal forms designated as ice II, III, IV, ... etc., up to 13 phases of cubic, hexagonal, tetragonal, monoclinic, and orthorhombic symmetries have been identified (26). The polymorphism of solid water is very complicated. Some of these ice forms are made under very high pressures, and water crystallizes into solid at temperatures above the normal melting or even boiling temperatures. Ice VII is formed above 10 G Pa (gigapascal) at 700 K (26).

When liquid water is frozen rapidly, the molecules have little chance of arranging into crystalline ice. The frozen liquid is called **amorphous ice** or **glassy ice**.

The basic relationships between nearest neighboring water molecules are the same in both  $I_h$  and  $I_c$ . All O atoms are bonded to four other O atoms by hydrogen bonds, which extend from an oxygen atom towards the vertices of a tetrahedron. A sketch of the crystal structure of hexagonal  $I_h$  is shown in Fig. 7 (27). In  $I_h$ , hydrogen positions are somewhat random due to thermal motion, disorder and exchanges.

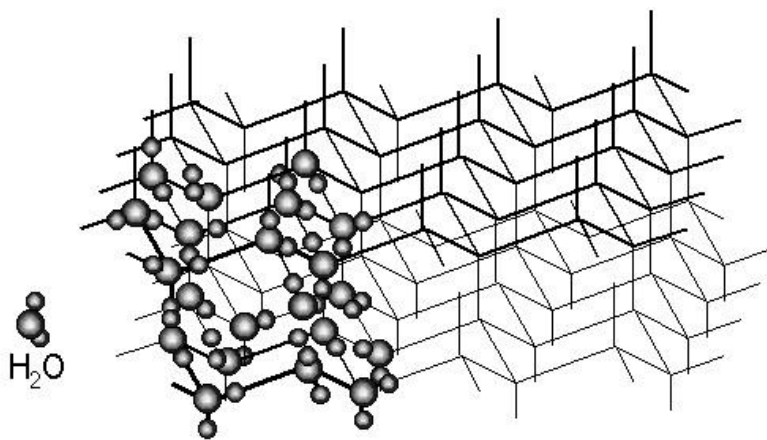


Fig. 7. Ordered crystal structure of ice, bond distance: O–H, 100 pm; H - - O, 175 pm; and O–H - - O, 275 pm.

For example, the hydrogen may shift between locations to form  $H_3O^+$  and  $OH^-$  ions dynamically throughout the structure. In this structure, bond angles or hydrogen-bond angles around oxygen atoms are those of the idealized tetrahedral arrangement of  $109.5^\circ$  rather than  $104.5^\circ$  observed for isolated molecules. Formation of the hydrogen bond in ice lengthens the O–H bond distance, 100 pm compared to 96 pm in a single water molecule. The diagram illustrates a crystal structure that is completely hydrogen bonded, except for the molecules at the surface.

Each O atom of hexagonal ice  $I_h$  is surrounded by four almost linear O–H - - O hydrogen bonds of length 275 pm, in a tetrahedral fashion. Each C atom of cubic diamond is also surrounded by four C–C covalent bonds of length 154 pm. Thus, the tetrahedral coordination can either be cubic or hexagonal, from a geometrical viewpoint. Indeed, the uncommon cubic ice and hexagonal diamond have been observed, giving a close relationship in terms of spatial arrangement of atoms between ice and diamond (26). Strong hydrogen bonds make ice hard, but brittle. The structure is related to its physical properties, which vary with temperature.

The pressure of  $H_2O$  vapor in equilibrium with ice is called the **vapor pressure of ice**, which decreases as the temperature decreases. At the triple point or  $0^\circ C$ , the pressure is

611.15 Pa. When ice is slightly overheated to 0.01° C, the pressure increases to 611.657 Pa. However, at this temperature, the vapor pressure of liquid water is lower. The vapor pressures of ice between 0° C and – 40° C are listed in Table 5 at 1° C interval. Various models can be used to estimate the vapor pressure at other temperatures. One method uses the Clausius-Clapeyron differential equation

$$\frac{dp}{dT} = \frac{H}{T \Delta V}$$

where  $p$  is the pressure,  $T$  is the temperature (K),  $H$  is the latent heat or **enthalpy** of phase transition, and  $\Delta V$  is the difference in volume of the phases. The enthalpy of sublimation for ice depends on the temperature. At the freezing point, the enthalpy of sublimation for ice is 51 (51.06 in Table 3) kJ mol<sup>-1</sup>, estimated from the vapor pressure at 0 and –1° C. The enthalpy of sublimation is required to overcome hydrogen bonding, dipole, and intermolecular attractions. The energy required in freeze-drying processes varies, depending on temperature and other conditions. Water in solutions and in food freezes below 0° C.

The number of hydrogen bonds is twice the number of water molecules, when surface water molecules are ignored. The energy required to separate water molecules from the solid is the enthalpy of sublimation (55.71 J mol<sup>-1</sup>). Half of this value, 26 kJ mol<sup>-1</sup>, is the energy to separate the H- -O linkages, and it translates into 0.26 eV, per H- -O bond. These values are close to those obtained by other means (25, 26, 28, 29, 30). Several factors contribute to this linkage, and the hydrogen-bond energy is less than 0.26 eV.

## B. Properties of Liquid Water

The macroscopic physical properties of this common but eccentric fluid at 298 K (25° C) are given in Table 6. Water has an unusually high melting and boiling points for a substance of molar mass of only 18 daltons. Strong hydrogen bonds and high polarity accounts for this.

**Table 5. Aqueous vapor pressure (Pa) in equilibrium with ice between 0 and –40° C**  
(at 0.01° C,  $p$  is 611.657 Pa)

$t$ (° C)	– 0 ■	– 1 ■	– 2 ■	– 3 ■	– 4 ■
– ■ 0	611.15	259.90	103.26	38.01	12.84
– ■ 1	562.67	237.74	93.77	34.24	
– ■ 2	517.72	217.32	85.10	30.82	
– ■ 3	476.06	198.52	77.16	27.71	
– ■ 4	437.47	181.22	69.91	24.90	
– ■ 5	401.76	165.30	63.29	22.35	7.20
– ■ 6	368.73	150.68	57.25	20.04	
– ■ 7	338.19	137.25	51.74	17.96	
– ■ 8	309.98	124.92	46.73	16.07	
– ■ 9	283.94	113.62	42.16	14.37	

Missing digits of  $t$ , ■, in the row are found in the column, and vice versa. These values are taken from the CRC Handbook of Chemistry and Physics (1).

**Table 6 Properties of liquid water at 298 K**

Heat of formation $\Delta H_f$	285.89 kJ mol <sup>-1</sup>
Density at 3.98° C	1.000 g cm <sup>-3</sup>
Density at 25° C	0.9970480 g cm <sup>-3</sup>
Heat capacity	4.17856 J g <sup>-1</sup> K <sup>-1</sup>
$\Delta H_{\text{vaporization}}$	55.71 kJ mol <sup>-1</sup>
Dielectric constant	80.
Dipole moment	6.24 × 10 <sup>-30</sup> C m
Viscosity	0.8949 mP? s <sup>-1</sup>
Velocity of sound	1496.3 m s <sup>-1</sup>
Volumetric thermal expansion coefficient	0.0035 cm <sup>3</sup> g <sup>-1</sup> K <sup>-1</sup>

The heat of formation is the energy released when a mole of hydrogen and half a mole of oxygen at 298 K and 1.00 atm react to give one mole of water at 298 K. This value differs from that for ice in Table 4 due to both temperature and phase differences. As temperature increases, the average kinetic energy of molecules increases, and this affects water's physical properties. For example, surface tension of water decreases, whereas the thermal conductance increases as the temperature increases. Heat capacity at constant pressure ( $C_p$ ), vapor pressure, viscosity, thermal conductance, dielectric constant, and surface tension in the temperature range 273–373 K (0–100°C) are given in Table 7.

**Table 7. Properties of liquid water in the range 273 – 373 K (0 – 100° C)**

Temp. $t$ (°C)	Heat capacity $C_p$ (J g <sup>-1</sup> K <sup>-1</sup> )	Viscosity (mPa s)	Thermal conductance (W K <sup>-1</sup> m <sup>-1</sup> )	Dielectric constant	Surface tension (mN m <sup>-1</sup> )
0	4.2176	1.793	561.0	87.90	75.64
10	4.1921	1.307	580.0	83.96	74.23
20	4.1818	1.002	598.4	80.20	72.75
30	4.1784	0.797	615.4	76.60	71.20
40	4.1785	0.653	630.5	73.17	69.60
50	4.1806	0.547	643.5	69.88	67.94
60	4.1843	0.466	654.3	66.73	66.24
70	4.1895	0.404	663.1	63.73	64.47
80	4.1963	0.354	670.0	60.86	62.67
90	4.2050	0.315	675.3	58.12	60.82
100	4.2159	0.282	679.1	55.51	58.91

-----  
More detailed data can be found in the CRC Handbook of Chemistry and Physics (1)

Liquid water has the largest heat capacity per unit mass of all substances. Large quantities of energy are absorbed or release when its temperatures changes. The large heat capacity makes water an excellent reservoir and transporter of energy. A large body of water moderates climate. The heat capacity  $C_p$  of water varies between 4.1 to 4.2 J g<sup>-1</sup> K<sup>-1</sup> (74 to 76 J mol<sup>-1</sup> K<sup>-1</sup>) even at temperature above 100° C and high pressure. The enthalpy of vaporization for water is also very large (55.71 kJ mol<sup>-1</sup> at 298 K). Thus, energy consumption is high for food processing when water is involved.

Water and aqueous solutions containing only low molar-mass solutes are typical Newtonian fluids for which the **shear stress** is proportional to **shear strain rate**. Viscosity is the ratio of shear stress to shear strain rate. On the other hand, viscosity of solutions containing high molar-mass substances depends on shear strain rate. For pure water, the viscosity decreases from 1.793 to 0.282 mPa s (millipascal seconds; identical to centipoise (cp)) as temperature increases from 0 to 100° C. Thus, the flow rate through pipes increases as water or solution temperature increases.

The dielectric constant of water is very large, and this enables water to separate ions of electrolytes, because it reduces the electrostatic attraction between positive and negative ions. Many salts dissolve in water. When an electric field is applied to water, its dipole

molecules orient themselves to decrease the field strength. Thus, its dielectric constant is very large. The dielectric constant decreases as temperature increases, because the percentage of molecules involved in hydrogen bonding and the degree of order decrease (28, 29). The measured dielectric constant also depends on the frequency of the applied electric field used in the measurement, but the variation is small when the frequency of the electric field is less than 100 MHz. The dielectric behavior of water allows water vapor pressure to be sensed by capacitance changes when moisture is absorbed by a substance that lies between the plates of a capacitor. These sensors have been developed for water activity measurement (31).

The light absorption coefficients are high in the infrared and ultraviolet regions, but very low in the visible region. Thus, water is transparent to human vision.

The variation of vapor pressure as a function of temperature is the bases for defining **water activities** of food. Liquid water exists between the triple-point and the critical-point temperatures (0 – 373.98°C) at pressures above the vapor pressures in this range.

As with ice, the vapor pressure of liquid water increases as the temperature increases. Vapor pressures of water (in kPa instead of Pa for ice in Table 5) between the triple and critical points, at 10°C interval, are given in Table 8. When the vapor pressure is 1.00 atm (101.32 kPa) the temperature is the boiling point (100°C). At slightly below 221°C, the vapor pressure is 2.00 atm. The critical pressure at the critical temperature, 373.98°C, is 217.67 atm (22,055 kPa). Above this temperature, water cannot be liquefied, and the phase is called **supercritical water**.

**Table 8. Vapor pressure (kPa) of liquid H<sub>2</sub>O between triple and critical points at every 10° C**

<i>t</i> ° C	0 ■ ■	1 ■ ■	2 ■ ■	3 ■ ■
■ 00	0.6113	101.32	1553.6	8583.8
■ 10	1.2281	143.24	1906.2	9860.5
■ 20	2.3388	198.48	2317.8	11279
■ 30	4.2455	270.02	2795.1	12852
■ 40	7.3814	361.19	3344.7	14594
■ 50	12.344	475.72	3973.6	16521
■ 60	19.932	617.66	4689.4	18665
■ 70	31.176	791.47	5499.9	21030
■ 80	47.375	1001.9	6413.2	22055*
■ 90	70.117	1254.2	7438.0	

\* Critical pressure at 373.98° C

Missing digits of *t*, ■, in the row are found in the column, and vice versa. Values from the CRC Handbook of Physics and Chemistry (2003) (1), which lists vapor pressure at 1° interval.

The partial pressure of H<sub>2</sub>O in the air at any temperature is the **absolute humidity**. When the air is saturated with water vapor, the **relative humidity** is 100%. The unsaturated vapor pressure divided by the vapor pressure of water as given in Table 8 at the temperature of the air is the **relative humidity**. The temperature at which the vapor pressure in the air becomes saturated is the **dew point**, at which dew begins to form. However when the dew point is below 273 K or 0°C, ice crystals (frost) begin to form. Thus, the relative humidity can be measured by finding the dew point. Dividing the vapor pressure at the dew point by the vapor pressure of water at the temperature of the air gives the relative humidity. The transformations between solid, liquid, and gaseous water

play important roles in hydrology and in the transformation of the environment on Earth. Phase transitions of water combined with the energy from the sun make the weather.

Density is a collective property and it varies with temperature, isotopic composition, purity, etc. The International Union of Pure and Applied Chemistry (IUPAC) has adopted the density of pure water from the ocean as the density standard. The isotopic composition of ordinary water is constant, and the density of pure water between 0 and 39° C extracted from (32) is given in Table 9.

**Table 9. The density of water (g / mL) as a function of temperature between 0 and 39° C (31).**

$t$ ° C	0 ■	1 ■	2 ■	3 ■
■ 0	0.9998426	0.9997021	0.9982063	0.9956511
■ 1	0.9999015	0.9996074	0.9979948	0.9953450
■ 2	0.9999429	0.9994996	0.9977730	0.9950302
■ 3	0.9999627	0.9993792	0.9975412	0.9947971
■ 4	0.9999750*	0.9992464	0.9972994	0.9943756
■ 5	0.9999668	0.9991016	0.9970480	0.9940359
■ 6	0.9999430	0.9989450	0.9967870	0.9936883
■ 7	0.9999043	0.9987769	0.9975166	0.9933328
■ 8	0.9998509	0.9985976	0.9962370	0.9929695
■ 9	0.9997834	0.9984073	0.9956511	0.9925987

Missing digits of  $t$ , ■, in the row are found in the column, and vice versa.

The density of cage-like ice  $I_h$ , due to 100% of its molecules involved in hydrogen-bonded is only 9% lower than that of water. This indicates that water has a high percentage of molecules involved in the transient and dynamic hydrogen bonding. The percentage of hydrogen-bonded water molecules in water decreases as temperature increases, causing water density to increase. As temperature increases the thermal expansion causes its density to decrease. The two effects cause water density to increase from 0 to 3.98°C, reaching its maximum of 1.0000 g mL<sup>-1</sup> and then decrease as temperature increases.

Incidentally at 8° C, the density of water is about the same as that at 0° C. At 25° C, the density decreases 0.3 % with respect to its maximum density, whereas at 100° C, it decreases by 4 %. Dense water sinks, and convection takes place when temperature fluctuates at the surface of lakes and ponds, bringing dissolved air and nutrients to various depths of waters for the organism living in them. On the other hand, the pattern of density dependence on temperature of water makes temperatures at the bottoms of lakes and oceans vary little if the water is undisturbed. When water freezes, ice begins to form at the surface, leaving the water at some depth undisturbed. Water at the bottom remains at 4°C preserving various creatures living in water.

When hydrogen-bonded to tissues and cells or in food, water has a unique order and structure, and the vapor pressure and density differ from those of pure water. Yet, the collective behavior of water molecules sheds some light regarding their properties in food, cells, tissues, and solutions.

## V. Chemical Properties of Water

Water is a chemical as is any substance, despite the confusion and distrust of the public regarding the term “chemical”. Thus, water has lots of interesting chemical properties. It

interacts intimately with components of food particularly as a solvent, due to its dipole moment and its tendency to form hydrogen bond. These interactions affect the chemical properties of nutrients, including their tendency to undergo oxidation or reduction, to act as acids or bases, and to ionize.

### **A. Water as a Universal Solvent**

Water is dubbed a universal solvent, because it dissolves many substances due to strong interactions between water molecules and those of other substances. Entropy is another driving force for a liquid to dissolve or mix with other substances. Mixing increases disorder or entropy.

#### **(a ) hydrophobic effect and hydrophilic effect**

Because of its large dielectric constant, high dipole moment and ability to donate and accept protons for hydrogen bonding, water is an excellent solvent for polar substances and electrolytes, which consist of ions. Molecules strongly interact with or love water molecules are **hydrophilic**, due to hydrogen bonding, polar-ionic or polar-polar attractions. Nonpolar molecules that do not mix with water are **hydrophobic** or **lipophilic**, because they tend to dissolve in oil. Large molecules such as proteins and fatty acids that have hydrophilic and hydrophobic portions are **amphipathic** or **amphiphilic**. Water molecules strongly intermingle with hydrophilic portions by means of dipole-dipole interaction or hydrogen bonding.

The lack of strong interactions between water molecules and lipophilic molecules or the nonpolar portions of amphipathic molecules is called the **hydrophobic effect**, a term coined by Charles Tanford (33). Instead of a direct interaction with such solutes, water molecules tend to form hydrogen-bonded cages around small nonpolar molecules when the latter are dispersed into water. Hydrogen-bonded water molecules form cages, called **hydrates** or **clathrates**, For example, the clathrate of methane forms stable crystals at low temperatures (34).

Nonpolar chains in proteins prefer to stay together as they avoid contact with water molecules. Hydrophilic and hydrophobic effects play important roles for the stability and state of large molecules such as enzymes, proteins, and lipids. Hydrophobic portions of these molecules stay together forming pockets in globular proteins. Hydrophilic and hydrophobic effects cause nonpolar portions of phospholipids, proteins, and cholesterol to assemble into bilayers or biological membranes (34).



## (b) Hydration of ions

Due to its high dielectric constant, water reduces the attractions among positive and negative ions of electrolytes and dissolves them. The polar water molecules coordinate around ions forming hydrated ions such as  $\text{Na}(\text{H}_2\text{O})_6^+$ ,  $\text{Ca}(\text{H}_2\text{O})_8^{2+}$ ,  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  etc. Six to eight water molecules form the first sphere of hydration around these ions. Fig. 8 is a sketch of the interactions of water molecules with ions.

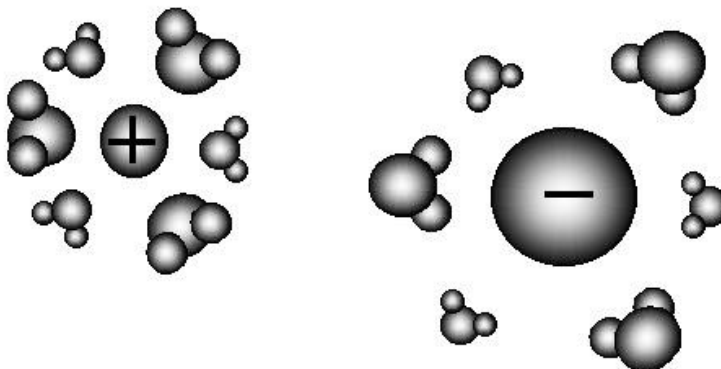


Fig. 8. The first hydration sphere of most cations  $\text{M}(\text{H}_2\text{O})_6^+$ , and anions  $\text{X}(\text{H}_2\text{O})_6^-$ . Small water molecules are below the plane containing the ions, and large water molecules are above the plane.

The water molecules point their negative ends of their dipoles towards positive ions, and their positive ends towards negative ions. Molecules in the hydration sphere constantly and dynamically exchange with those around them. The number of hydrated-water molecules and their lifetimes have been studied by various methods. These studies reveal that the hydration sphere is one-layer deep, and the life times of these hydrated-water molecules are in the order of picoseconds ( $10^{-12}$  s). The larger negative ions also interact with the polar water molecules, not as strong as those of cations. The presence of ions in the solution changes the ordering of molecules even if they are not in the first hydration sphere (9).

The hydration of ions releases energy, but breaking up ions from a solid requires energy. The amounts of energy depends on the substance, and for this reason, some are more soluble than others. Natural waters in the ocean, streams, rivers and lakes are in contact with minerals and salts. The concentrations of various ions depend on the solubility of salts (35) and the contact time.

Drinking water includes all waters used in growth, processing, and manufacturing of food. J. De Zuane divides ions in natural water into four types in *The Handbook on Drinking Water Quality* (5).

Type A includes arsenic, barium, cadmium, chromium, copper, fluoride, mercury, nitrate, nitrite, and selenium ions. They are highly toxic, yet abundant.

Type B includes aluminum, nickel, sodium, cyanide, silver, zinc, molybdenum, and sulfate ions. Their concentrations are also high, but they are not very toxic.

Type C consists of calcium, carbonate, chloride, iron, lithium, magnesium, manganese, oxygen, phosphate, potassium, silica, bromine, chlorine, and iodine and ozone. They are usually present at reasonable levels.

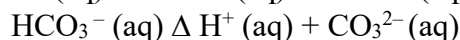
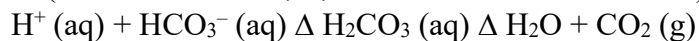
Type D ions are present usually at low levels: antimony, beryllium, cobalt, tin, thorium, vanadium and thallium.

Most metals are usually present in water as cations, with a few as anions. However, some chemical analyses may not distinguish their state in water. The most common anions are chloride, sulfate, carbonate, bicarbonate, phosphate, bromide, iodide, etc. Toxicity is a concern for ions in water, but some of these ions are essential for humans.

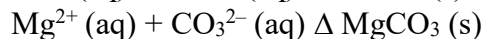
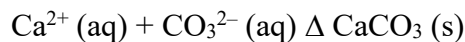
Pure water has a very low electric conductivity, but ions in solutions move in an electric field making electrolyte solutions highly conductive. The conductivity is related to total dissolved solids (TDS), salts of carbonate, bicarbonate, chloride, sulfate, and nitrate. Sodium, potassium, calcium and magnesium ions are often present in natural waters because their soluble salts are common minerals in the environment. The solubilities of clay (alumina), silicates, and most common minerals in the Earth crust, are low.

### (c) Hard waters and their treatments

Waters containing plenty of dissolved  $\text{CO}_2$  ( $\text{H}_2\text{CO}_3$ ) are acidic and they dissolve  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . Waters with dissolved  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  are called **temporary hard waters** as the hardness can be removed by boiling, which reduces the solubility of  $\text{CO}_2$ . When  $\text{CO}_2$  is driven off, the solution becomes less acidic due to the following equilibria (the double arrows,  $\Delta$ , indicate reversible reactions):

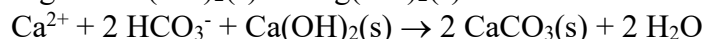
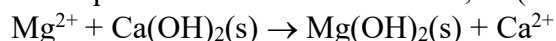


Reducing the acidity increases the concentration of  $\text{CO}_3^{2-}$  and solids  $\text{CaCO}_3$  and  $\text{MgCO}_3$  precipitate:

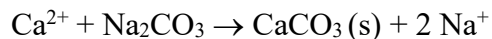


Water containing less than  $50 \text{ mg L}^{-1}$  of these substances is considered soft;  $50\text{-}150 \text{ mg L}^{-1}$  moderately hard;  $150\text{-}300 \text{ mg L}^{-1}$  hard; and more than  $300 \text{ mg L}^{-1}$  very hard.

For the **lime treatment**, we determine the amount of dissolved  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  first; and then add an equal number of moles of lime,  $\text{Ca}(\text{OH})_2$ , to remove them by these reactions:



**Permanent hard waters** contain sulfate ( $\text{SO}_4^{2-}$ ) ions with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Calcium ions,  $\text{Ca}^{2+}$ , of the sulfate solution can be removed by adding sodium carbonate:



Hard waters cause scales or deposits to build up in boilers and pipes, and they are usually softened by ion exchange with resins or zeolites. In these processes, the calcium and magnesium ions are taken up by the zeolite or resin that releases sodium or hydrogen ions into the water. Reverse osmosis has also been used to soften hard water.

However, water softening replaces desirable calcium and other ions by sodium ions. Thus, soft waters are not suitable drinking waters. Incidentally, bakers use hard water because the calcium ions strengthen the gluten proteins in dough mixing. Some calcium salts are added to dough to enhance bread quality.

#### (d) Properties of aqueous solutions

Waters containing dissolved substances are aqueous solutions; their physical properties differ from those of pure water. For example, at the same temperature, the H<sub>2</sub>O vapor pressures of solutions are lower than that of pure water, resulting in boiling point elevation (higher), freezing point depression (lower) and osmotic pressure.

Several ways can be used to express concentrations: part per million (ppm), percent, moles per liter, mole fraction, etc. The mole fraction of water is the fraction of water molecules among all molecules and ions in the system. The vapor pressure of an ideal solution,  $P_{\text{solution}}$ , is the vapor pressure of water (at a given temperature),  $P^{\circ}_{\text{water}}$ , modified by the mole fraction  $X_{\text{water}}$ .

$$P_{\text{solution}} = X_{\text{water}} P^{\circ}_{\text{water}} \quad (X_{\text{water}} < 1)$$

If the solute has a significant vapor pressure,  $P_{\text{solute}}$  is also modified by its mole fraction,

$$P_{\text{solute}} = X_{\text{solute}} P^{\circ}_{\text{solute}}$$

For non-ideal solutions, in which water and solute strongly interact, the formulas require modifications. A practical method is to use an **effective mole fraction**  $X$  defined by:

$$P_{\text{solution}} / P^{\circ}_{\text{water}} = X$$

In any case, the vapor pressures of solutions containing nonvolatile electrolytes are lower than those of pure water at their corresponding temperature.

Phase transitions take place when the vapor pressures of the two phases are the same. Because solutions' vapor pressures are lower, their melting points are lower but their boiling points are higher. The difference in temperature,  $\Delta T$ , is proportional to the concentrations of all solutes,  $m_{\text{all-solute}}$  (molality),

$$\Delta T = K m_{\text{all-solute}}$$

where  $K$  is either the molar boiling point elevation constant,  $K_b$ , or the molar freezing point depression constant  $K_f$ . For water,  $K_f = 1.86 \text{ K L kg}^{-1}$ , and  $K_b = 0.52 \text{ K L kg}^{-1}$ . Due to ionization of electrolytes, positive and negative ions should be treated as separate species and all species should be included in  $m_{\text{all-solute}}$ .

The tendency of water molecules from a dilute solution to diffuse into a more concentrated solution, through semipermeable membranes, has a measurable quantity called **osmotic pressure**,  $\pi$ , which is proportional to the concentration (mol per kg of water) of all dissolved species,  $m_{\text{all-solute}}$  in mol kg<sup>-1</sup> and temperature  $T$  in K,

$$\pi = -m_{\text{all-solute}} R T$$

where  $R$  is the gas constant  $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ . Water molecules diffuse from pure water ( $\pi = 0$ ) into the solution, and the osmotic pressure is therefore given as a negative value here. Theoretically, a solution with  $m_{\text{all-solute}} = 1.0 \text{ mol kg}^{-1}$  of water,  $\pi = -2477 \text{ J kg}$  or  $-2.477 \text{ kJ kg}$  at 298 K. Note  $m_{\text{all-solute}} = m i$ ; ( $i$  being the number of ions produced by the solute) in the van't Hoff equation, which is often used in other literature.

Solutions having the identical osmotic pressure are isotonic. Applying more pressure to a solution to compensate for the osmotic pressure causes water molecules to diffuse through membranes, generating pure or fresh waters. This process is called **reverse**

**osmosis**, and it has been used to soften water or desalinate seawater, converting it to fresh water.

The lowering of vapor pressure and the osmotic pressure of solutions play important roles in hydration and dehydration of food and in living cells. Solutions containing proper concentrations of nutrients and electrolyte have been used to medically treat dehydrated patients. J.R. Cade and his coworkers applied these principles to formulate drinks for athletes; he and his coworkers were credited as the inventor of the sports drink Gatorade (36). The concept of a balanced solution for hydration became a great business decades after its invention.

## B. Acidity and Alkalinity of Water

Acidity and alkalinity are also important characteristics of water due to its dynamic self-ionization equilibrium,

$$\text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{H}^+ + \text{OH}^-, \quad K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ at } 298 \text{ K and } 1 \text{ atm}$$
where  $[\text{H}^+]$  and  $[\text{OH}^-]$  represent the molar concentrations of  $\text{H}^+$  (or  $\text{H}_3\text{O}^+$ ) and  $\text{OH}^-$  ions, respectively, and  $K_w$  is called the **ion product of water**, (see tables in ref. 1 and 36). Values of  $K_w$  under various conditions have been evaluated theoretically (37, 38). Solutions in which  $[\text{H}^+] = [\text{OH}^-]$  are said to be neutral. At 298 K, for a neutral solution,

$$\text{pH} = -\log [\text{H}^+] = \text{pOH} = -\log [\text{OH}^-] = 7 \quad (\text{at } 298 \text{ K})$$
The  $\text{H}^+$  ions or protons dynamically exchange with protons in other water molecules. The self-ionization and equilibrium are present in all aqueous solutions, including acid and base solutions, as well as in pure water. Water is both an acid and a base.

Strong acids such as  $\text{HClO}_4$ ,  $\text{HClO}_3$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  ionize completely in their solutions to give  $\text{H}^+$  ( $\text{H}_3\text{O}^+$ ) ions and anions:  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{HSO}_4^-$ , respectively. Strong bases such as  $\text{NaOH}$ ,  $\text{KOH}$ , and  $\text{Ca}(\text{OH})_2$  also ionize completely giving  $\text{OH}^-$  ions and  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  ions respectively. In an acidic solution,  $[\text{H}^+]$  is greater than  $[\text{OH}^-]$ . In a 1.0 mol  $\text{L}^{-1}$   $\text{HCl}$  solution,  $[\text{H}^+] = 1.0 \text{ mol L}^{-1}$ ,  $\text{pH} = 0$ .

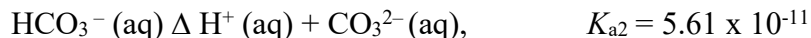
Weak acids such as formic acid,  $\text{HCOOH}$ , acetic acid ( $\text{CH}_3\text{COOH}$ ), ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ), oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ), carbonic acid ( $\text{H}_2\text{CO}_3$ ), benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ), malic acid ( $\text{C}_4\text{H}_6\text{O}_5$ ), lactic acid  $\text{H}_3\text{CCH}(\text{OH})\text{COOH}$ , and phosphoric acid ( $\text{H}_3\text{PO}_4$ ) also ionize in their aqueous solutions, but not completely. The ionization of acetic acid, is represented by the equilibrium,

$$\text{CH}_3\text{COOH} (\text{aq}) \rightleftharpoons \text{H}^+ (\text{aq}) + \text{CH}_3\text{COO}^- (\text{aq}), \quad K_a = 1.75 \times 10^{-5} \text{ at } 298 \text{ K}$$
where  $K_a$  is the acid dissociation constant.

The solubility of  $\text{CO}_2$  in water increases with its ( $\text{CO}_2$  partial) pressure, according to Henry's law, and the chemical equilibria for the dissolution is,

$$\text{H}_2\text{O} + \text{CO}_2 (\text{g}) \rightleftharpoons \text{H}_2\text{CO}_3 (\text{aq})$$
Of course,  $\text{H}_2\text{CO}_3$  dynamically exchanges  $\text{H}^+$ , and  $\text{H}_2\text{O}$  with other water molecules, and this weak diprotic acid ionizes in two stages with their acid constants,  $K_{a1}$  and  $K_{a2}$ .

$$\text{H}_2\text{O} + \text{CO}_2 (\text{aq}) \rightleftharpoons \text{H}^+ (\text{aq}) + \text{HCO}_3^- (\text{aq}), \quad K_{a1} = 4.30 \times 10^{-7} \quad (\text{at } 298 \text{ K})$$



Constants  $K_{a1}$  and  $K_{a2}$  increase with temperature. At 298 K, the pH of a solution containing  $0.1 \text{ mol L}^{-1} \text{ H}_2\text{CO}_3$  is 3.7, acidophilic organisms may grow, but most pathogenic organisms are neutrophiles and they cease growing. Soft drinks contain other acids – citric, malic, phosphoric, ascorbic acids etc; they lower the pH further.

Ammonia and many nitrogen-containing compounds are weak bases. The ionization equilibrium of  $\text{NH}_3$  in water and the base dissociation constant  $K_b$  are,



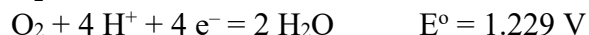
Other weak bases react with  $\text{H}_2\text{O}$  similarly.

The ionization or dissociation constants of inorganic and organic acids and bases are extensive, and they have been tabulated in various books (39, 40, 41).

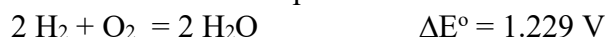
Amino acids and proteins contain acidic and basic groups. At some specific pH called the **isoelectric point**, they carry no charge, but exist as zwitterions. For example, the isoelectric point for glycine is  $\text{pH} = 6.00$  and it exists as the zwitterion  $\text{H}_2\text{C}(\text{NH}_3^+)\text{COO}^-$ .

### C. Oxidation-Reduction Reactions in Water

Oxidation of hydrogen by oxygen not only produces water, but also releases energy. At the standard conditions, the electrochemical half reaction equations are:

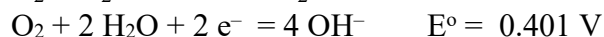
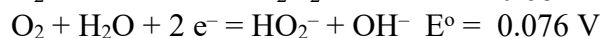
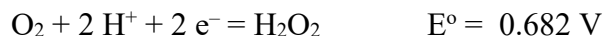
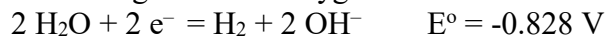


The cell reaction and the cell potential at the standard condition for it are:



Proper setups for harvesting this energy are the goals of hydrogen-fuel-cell technology. The cell potential  $\Delta E$  for non-standard conditions depends on pH and temperature. Its value is related to the energy released in the reaction. A plot of  $\Delta E$  versus pH yields a Pourbaix diagram, which is useful to evaluate the stability of various species in water. Water can be a reducing or oxidizing reagent, because it offers protons or electrons. Applying a voltage to pass electrons through a chemical cell decomposes water by electrolysis.

Waters containing dissolved oxygen cause additional reactions, for example:



At the proper conditions, a suitable chemical reaction driven by the potential takes place.

Oxidation-reduction reactions involving water usually are due to proton or electron transfer. These oxidation-reduction reactions occur for the growth, production, manufacture, digestion, and metabolism of food.

Water participates in oxidation-reduction reactions in many steps of photosynthesis, resulting in the fixation of CO<sub>2</sub> into biomolecules, releasing oxygen atoms of water as O<sub>2</sub>. Engineering a new generation of plants with greater photosynthetic capacity facing lack of waters challenges geneticists (42) and botanists. We now understand photosynthesis to great details, from the studies by many scientists. Photosynthetic reactions are related to food production, but they are so complex that we can only mention them (43).

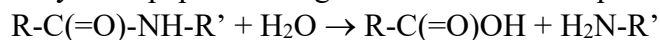
The oxidation-reduction reactions of water cause corrosion on metal surfaces. Not only deterioration of facilities is very costly for the food industry, corrosion of pipes results in having toxic metal ions Cu<sup>2+</sup> and Pb<sup>2+</sup> in drinking water. The concern of lead ions in drinking water led the Environmental Protection Agency to ban the use of high-lead solders for water pipes. These reactions are electrochemical processes. Galvanic effects, high acidity, high flow rate, high water temperature, and the presence of suspended solids accelerate corrosion, as do lack of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in purified waters. The formation of scales protects the metal surface. However, balancing the clogging against surface protection of pipes is a complicated problem, requiring scientific testing and engineering techniques for a satisfactory solution.

#### **D. The Hydrogen Bond and Chemical Reactions**

Enzymes are mostly large protein molecules, and they are selective and specific catalysts responsible for most of reactions in biological bodies. Folding of the long protein provides specific 3-dimensional selective pockets for their substrates. The pockets not only fix the substrates in position, they also weaken certain bonds to facilitate specific reactions. This is the mechanism by which enzymes select their substrates and facilitate their specific reactions.

Hydrogen bond strength is stronger in nonaqueous media than in aqueous solutions as the charge densities on the donor and acceptor atoms increase (44). Hydrogen bonds between the enzyme and its substrate can be stronger than those in an aqueous environment, thus speeding up the reaction rate even further.

The hydrolysis of peptide linkage is the reaction of a protein with water,



This type of reaction can be catalyzed by acids, bases, and enzymes.

#### **VI. Water Activity**

Water is a nutrient and a component in food groups: grains, meat, dairy, fruits and vegetables. Furthermore, major nutrients such as carbohydrates, proteins, water-soluble vitamins, and minerals are hydrophilic. Even parts of fat or lipid molecules are hydrophilic, but the alkyl chains of fats and proteins experience the hydrophobic effect in an aqueous environment. (45).

Foodstuffs interact with water by means of polar, hydrogen-bonding and hydrophobic interactions. The results of these interactions change the chemical potential (properties)

of water. Foodstuffs dissolve in or absorb water. Thus, water within food may be divided into bound water, affected water, and free water in the order of their interaction strength. The bound water molecules are similar to those in the first hydration sphere of ions, and those close to the first sphere are affected water molecules. Further away from the interface are free water molecules. The structure and properties of the first two types change. Interaction of water with dietary fiber is an example (46). Thus, properties of water in food are different from those of pure water.

Water molecules in both liquid and vapor phases can participate in hydration reactions. At equilibrium in a system with two or more phases, their vapor pressure or chemical potential,  $\mu$ , must be equal. The chemical potential,  $\mu$ , of a solution or water-containing foodstuff must be equal at a given temperature  $T$ , and

$$\mu = \mu_w + R T \ln (p / p_w),$$

where  $R$  is the gas constant ( $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $p$  is the vapor pressure of the solution or of water in foodstuff, and  $p_w$  is the vapor pressure of pure water at the same temperature. The ratio  $p / p_w$  is called the **water activity**  $a_w (= p / p_w)$ , which is related to the water chemical potential of water in solutions or in the foodstuff. For ideal solutions and for most moist foods,  $a_w$  is less than unity,  $a_w < 1.0$  (31).

Both water activity and relative humidity are fractions of the vapor pressure of pure water. Methods for their measurements are the same. We have mentioned the measurement by changes in capacitance earlier. Water contents have a sigmoidal relationship with water activities,  $a_w = 1.0$  for infinitely dilute solutions,  $a_w > 0.7$  for dilute solutions and moist foods and  $a_w < 0.6$  for dry foods. Of course, the precise relationship depends on the material in question. In general, if the water vapor of the atmosphere surrounding the food is greater than the activity of the food, water is absorbed. Otherwise, dehydration takes place. The water activity reflects the combined effects of water-solute, water-surface, capillary, hydrophilic and hydrophobic interactions. The water activity of a foodstuff is a vital parameter, because it affects its texture, taste, safety, shelf life, and appearance.

Furthermore, controlling water activity, rather than water content is important. When  $a_w < 0.9$ , most molds are inhibited. Growth of yeasts and bacteria also depends on  $a_w$ . Microorganisms cease growing if  $a_w < 0.6$ .

## VII Water Potential

Similar to water activity in food, **water potential** is a term used in plant, soil, and crop sciences. Water potential, represented by  $\Psi$  (psi) or  $\Psi_w$ , is a measure of the free energy of water in a system: soil, material, seeds, plants, roots, leaves, or an organism. Water potential is the difference between the chemical potential of pure water and water in the system at the same temperature. Pure water has the highest free energy:  $\Psi = 0$  for pure water by convention, and  $\Psi < 0$  for solutions. Water diffuses from high potential to low potential. Physiological processes decrease as the water potential decreases.

In general, water potential,  $\Psi_w$ , is a combined effect of osmotic ( $\Psi_s$ ), matrix (interface and water binding  $\Psi_m$ ), turgor ( $\Psi_t$ ) pressures, and gravity ( $\Psi_g$ ).

$$\Psi_w = \Psi_s + \Psi_m + \Psi_t + \Psi_g$$

Osmotic pressure,  $\Psi_s$ , is always present due to solutes in the fluids. The metric pressure,  $\Psi_m$ , is related to bound-, affected- and free-waters in the system. The outwardly directed pressure extended by the swelling protoplast against the wall is called turgor pressure,  $\Psi_t$ . Usually, this term is insignificant until the cell is full, and at such point,  $\Psi_t$  increases rapidly and stops when  $\Psi_w = \Psi_t$ . Otherwise, the cell ruptures. The mechanical rigidity of succulent plant parts, the opening of stomata and the blossom are usually the results of turgor pressure. In systems such as tall plants and soil science, pressure due to the gravitational pull of water,  $\Psi_g$ , is also included in the water potential.

For example, the water potential of potato tissues can be measured by incubating them in a series of solutions of known osmotic pressures. The potato will neither lose nor gain water if the osmotic pressure of the solution equals the water potential of potato tissues. The osmotic pressure ( $\pi = -m R T$ ) may be evaluated from a known concentration  $m$ , using the equation given earlier. Instead of energy units, water potential is often expressed in units of pressure (megapascal, MPa), which is derived by dividing the energy by the molar volume (0.018 L mol<sup>-1</sup> for H<sub>2</sub>O) of water (47).

There are many other methods for water potential measurements depending on the system: soil, leaf, stem, organism, etc. The soil water potential is related to the water available for the plants growing on the soil. Water potential of a plant or leaf indicates its health or state with respect to water. Thus, water potential is a better indicator for plant, agriculture, irrigation, and environmental managements than water content. Water moves through plants because

$$\Psi_{\text{water}} = 0 > \Psi_{\text{soil}} > \Psi_{\text{root}} > \Psi_{\text{stem}} > \Psi_{\text{leaf}}$$

Thus, the concept of water potential and water activity are very useful in growth, manufacture, handling, storage, and management of food.

## VIII. Living Organisms in Water

The closer we look, the more we see. Living organisms on Earth are so complicated that their classification and phylogeny are still being studied and revised. New relationships are proposed to modify the five kingdoms proposed by Robert Whittaker in 1969. Nevertheless, most of the earliest unicellular living organisms in the Monera, and Protista kingdoms are still living in water. Both the numbers of species and individuals are staggering. For example, photosynthesis by algae in oceans consumes more CO<sub>2</sub> than that by all plants on land. Algae were probably present on Earth before other organisms. Many phyla (divisions) of fungi, plantae, and animalia kingdoms also make water their homes. Both numbers and species of organisms living in water are probably more than those on land. The subject on living organisms in water is fascinating, but we can only mention some fundamentals about their relationships to water here. Certainly, every aspect of living organisms in water is related to food, because Homo sapiens is part of the food chain, if not at the top of it.

All life requires energy or food. Some living organisms receive their energy from the sun whereas others get their energy from chemical reactions in the aquatic media. Chemical



reactions are vital during their lives. For example, some bacteria derive energy by catalyzing the oxidation of iron sulfide,  $\text{FeS}_2$ , to produce iron ions  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and elemental sulfur. Water is the oxidant, which in turn reduces oxygen (48). Chemical reactions provide energy for bacteria to sustain their lives and to reproduce. Factors affecting life in water are minerals, solubility of the mineral, electrochemical potentials of the material, acidity (pH), sunlight, dissolved oxygen level, presence of ions, chemical equilibria, etc. Properties of water influence life in general, and in the aquatic system in particular. As the population grows, aquaculture probably will be seen as a more efficient way of supplying protein for the ever-increasing population.

Regarding drinking water, we are concerned with aquatic organisms invisible to the naked eye. Pathogenic organisms present in drinking water cause intestinal infections, dysentery, hepatitis, typhoid fever, cholera, and other illnesses. Pathogens are usually present in waters contaminated with human and animal wastes that enter the water system via discharge, run offs, flood, and accidents at sewage treatment facilities. Insects, rodents, and animals can also bring bacteria to the water system (49, 50). Testing for all pathogenic organisms is impossible, but some organisms have common living conditions to some pathogenic bacteria. Thus, water testing can use these harmless bacteria as indicators for drinking water safety.

## IX. Water Resource, Supply, Treatment, and Usage

About 70% of the Earth surface is covered with water, but only about 2% is covered by fresh water. Ocean waters are salty, and only the small percentages that is fresh water resources (lakes, rivers, and underground). Fresh water is needed for drinking, food, farming, washing, and manufacturing.

When salty water freezes, the ice so formed contains very little salt, if any. Thus, nearly all ice, including the massive ice at the polar cap, is fresh water. In fact, the ice cap in the Antarctic contains a lot of fresh-water ice, but that cannot be considered a water resource.

Hydrologists, environmentalists, and scientists, engineers, sociologists, economists, and politicians are all concerned with problems associated with water resources. Solutions to these problems require experts and social consensus.

## X. Subcritical and Supercritical Waters

Waters at temperatures between the normal boiling and critical points (0 to  $373.98^\circ\text{C}$ ) are called **subcritical waters**, whereas the phase above the critical point is **supercritical water**. In the 17<sup>th</sup> century, Denis Papin (a physicist) generated high-pressure steam using a closed boiler, and thereafter pressure canners were used to preserve food. Pressure cookers were popular during the 20<sup>th</sup> century. Analytical chemists have used subcritical waters to extract chemicals from solids for analysis since 1994 (51).

Water vapor pressures up to its critical point are given in Table 8, but data on polarity, dielectric constant, surface tension, density and viscosity above  $100^\circ\text{C}$  are scarce. In

general, these properties decrease as the temperature increases. In fact, some drop dramatically for supercritical water. On the other hand, some of them increase with pressure. Thus, properties of sub- and super-critical waters can be manipulated by adjusting temperature and pressure to attain desirable properties.

As the polarity and dielectric constant decrease, water becomes an excellent solvent for non-polar substances such as those for flavor and fragrance. However, foodstuffs may degrade at high temperatures. Applications of sub- and super-critical water are relatively recent events, but applications of supercritical CO<sub>2</sub> (critical temperature 32°C) for chemical analyses started in the 1980s, and investigations of supercritical water followed. However, research and development have been intensified in recent years (52). Scientists and engineers explore the usage of supercritical water for waste treatment, polymer degradation, pharmaceutical manufacturing, chromatographic analysis, nuclear reactor cooling, etc. Significant advances have also been made in material processing, ranging from fine particle manufacture to the creation of porous materials.

Water has been called a green solvent compared to the polluting organic solvents. Sub- and super-critical waters have been explored as replacement of organic solvents in many applications including the food industry (53). However, supercritical water is very reactive, and it is corrosive for stainless steels that are inert to ordinary water. Yet, the application of sub- and super-critical waters is a wide-open field.

## **XI Postscript**

Water, ice, and vapor are collections of H<sub>2</sub>O molecules, whose characteristics determine the properties of all phases of water. Together and in concert water molecules shape the landscape, nurture lives, fascinate poets, and captivate scientists. Human efforts in understanding water have accumulated a wealth of science applicable in almost all disciplines, while some people take it for granted.

Water molecules are everywhere, including outer space. They not only intertwine with our history and lives, they are parts of us. How blessed we are to be able to associate and correlate the phenomena we see or experience to the science of water.

An article has a beginning and an end, but in the science of water, no one has the last word, as research and exploration, including its presence in outer space, on water continue (54). Writing this article induced my fascination on this subject, and for this reason, I am grateful to Professors Wai-kit Nip, Lewis Brubacher, and Peter F. Bernath for their helpful discussions and encouragement.

### **References, Tables, and Figures:**

See waterref.txt, watertab.rtf, and waterfig.ppt