Chapter 2
Life-Forming Role of Water in the Latest Discoveries and Hypotheses

Abstract The analytical review about life-forming role of water in conjunction with its unique properties which are predicated upon water structure peculiarities has been performed. The water role has been investigated from the perspective of different archebiosis scenarios on the Earth. Special attention has been paid to the isotopic water composition and deuterium influence on water structure, its properties and destruction of deoxyribonucleic acid. The isotopic composition and properties of heavy, light and ubiquitous water have been examined.

Keywords Water properties · Water structure · Isotopic water composition · Deuterium · Protium · Heavy water · Light water · Deoxyribonucleic acid

2.1 Unique Properties of Water

Throughout the entire history of our planet's existence, water has affected all aspects of the globe. It is this main building material, and the environment which contains it, that ensures the propagation and evolution of life on Earth.

For many centuries, scientists have studied this chemical substance, composed of the simple formula, H_2O, and known as one of the smallest and lightest molecules. Despite its simplicity and size, water somehow plays the main role in all biological processes and is considered "the matrix of life". The large heat capacity, high heat conduction and enormous amount of water in organisms contributes to heat regulation and prevents local temperature fluctuations, thereby enabling us to more easily control our body temperature. The high latent heat of evaporation ensures resistance to dehydration and high cooling in evaporation. Water, due to the polarity of its molecules, its high dielectric constant and its small sized molecules, is a good solvent primarily for polar ionic compounds and salts. It has unique properties of hydration with respect to biological macromolecules (especially to proteins and nucleic acids), which determine their three-dimensional structures and, consequently, functions in the solution. This hydration causes gels to form, which can be reversibly subjected to the sol–gel transition lying behind many cellular mechanisms.

Water is ionized and secures a light flow of proton exchange and is thereby conducive to the variety of ionic interactions in biology. "Water is incredibly multi-faceted, no other liquid has this property", says F. Gaiger, a leading water expert from Dortmund University. He believes that "… the world of liquids has been divided

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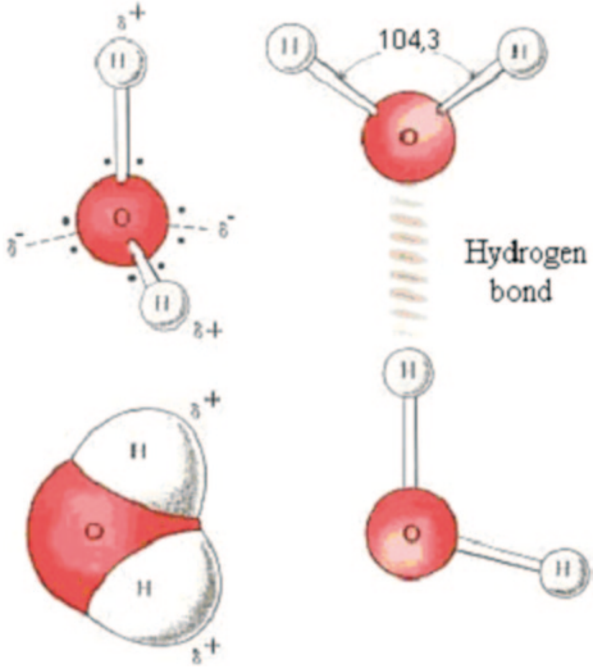


Fig. 2.1 Formation of hydrogen bonding

into two parts. On the one hand—water, on the other—all other substances". To this day there are a number of fundamental questions with no conclusive answers. Why does this substance behave, in many respects, atypically? Why does water in its crystalline state, i.e. in the form of ice, have so many "faces"—15 [1]?

The complicated behavior of this substance is determined by the structure of its molecules (Fig. 2.1). In the water molecule, two atoms of hydrogen and an atom of oxygen are arranged at an angle of 104.3° to each other. Owing to their electric polarity, both water molecules may create a special link between themselves; positive partial charges on hydrogen atoms and negative charges on oxygen atoms attract each other, forming hydrogen bridges. This link is 20 times weaker than the one which connects atoms of hydrogen and oxygen inside a molecule, but it exceeds the force of the normal attraction between the molecules, the Van der Waals force, by 60 times. The presence of the hydrogen bond in the water is necessary, but it is an insufficient condition for explaining its main properties. While the hydrogen bond is a necessary component of the water molecule, it alone does not represent the main properties of water. This can only be done when the structure of water is viewed as a single system [2].

Liquid Water In terms of statistics, particles of water in a liquid state form three and a half hydrogen bridges with their neighbors. These bridges collapse and line up again at a periodicity of a billionth of a fraction of a millisecond. In 1916, new notions about the structure of a liquid were proposed. The first X-ray structural

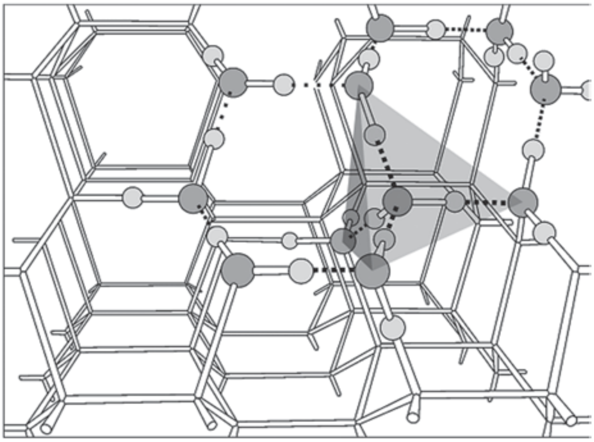


Fig. 2.2 Crystalline structure of ice

investigations of water were carried out in 1922 by Dutch scientists W. Keese and J. de Smedt. They proved that liquid water is characterized by the ordered arrangement of water molecules, i.e., water has a certain regular structure. The water structure in a living organism in many ways resembles the crystalline structure of ice (Fig. 2.2).

Special "adhesiveness" of a molecule is a reason why H_2O remains liquid at an extreme temperature of 100 °C. Chemically kindred materials in this sense go through heat at the maximum 25 °C [1]. Every water molecule in the crystalline structure of ice is involved in the formation of four hydrogen bonds directed to the apexes of the tetrahedron (Fig. 2.3). The tetrahedral center contains an oxygen atom, and two apexes each have a hydrogen atom whose electrons are involved in the formation of a covalent bond with the oxygen atom. Two remaining apexes are occupied by pairs of valence electrons from the oxygen atom, which do not take part in the formation of intramolecular links. In the interaction of the proton of one molecule with a lone pair of oxygen electrons from the other molecule, a hydrogen bond appears weaker than the intermolecular link but sufficiently powerful to hold together neighboring water molecules. Every molecule may simultaneously form four hydrogen bonds with other molecules at strictly definite angles, equaling 109°28′. These bonds are directed to the apexes of the tetrahedral, which does not allow them at freezing to form a dense structure.

The first theory on the structure of water was put forward by English researchers J. Bernal and R. Fowler. They created a concept about the tetrahedral structure of water and defined the role of hydrogen bonds in water. It was found that there are covalent and hydrogen bonds in water. The covalent bonds do not break in phase transitions of the water: water–steam–ice. Only electrolysis, a process of heating water on iron and similar processes, break water covalence bonds. Hydrogen bonds are 24 times weaker than covalence bonds. In melting ice and snow, hydrogen bonds partially remained in the water, and in a steam state they are all broken (Fig. 2.4) [2].

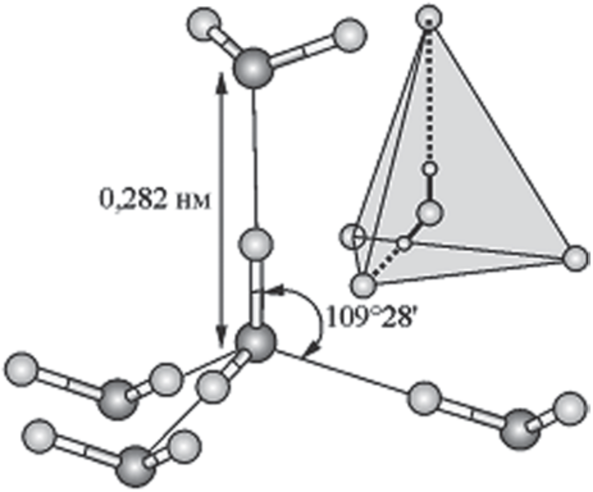


Fig. 2.3 Tetrahedral structure of water molecules

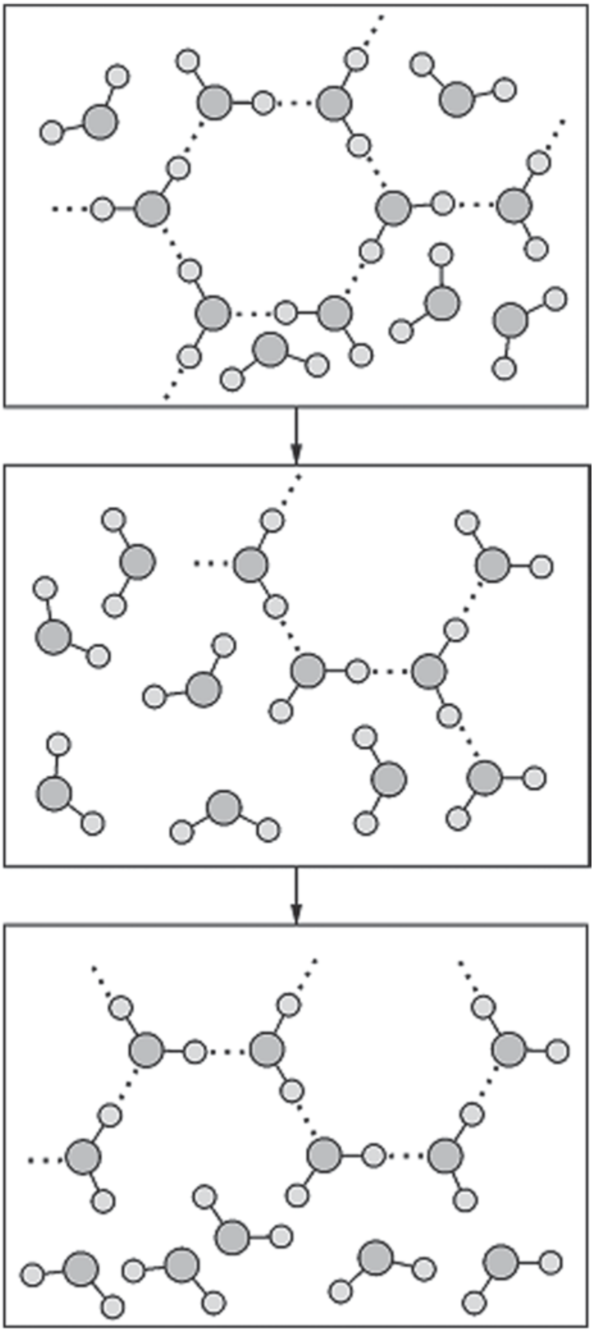
Later, an idea was developed, according to which liquid water was proposed as a pseudocrystal (Fig. 2.5); in it, individual tetrahedral molecules of H_2O are said to be linked to each other by directional hydrogen bonds, forming hexagonal structures such as in the ice structure.

Ice Ih In the abbreviation *Ih*, the letter *h* denotes hexagonal. This type of ice is drifting in seas and oceans; it is one of 15 types of the crystalline states of the water known today, and this shape is encountered on the Earth more often than others. The molecules are arranged in such a way that each element has 4 neighbors to which they are linked by hydrogen bridges. As a result, a lattice with a hexagonal base is formed by oxygen atoms [1].

X-ray crystallographic research carried out by J.P. Morgan and B.E. Warren showed that a structure like that of ice is inherent in water. In water, like in ice, every atom of oxygen is surrounded by oxygen atoms as in the tetrahedron. The distance between neighboring molecules is not identical. At 25 °C, every water molecule in the framework has one neighbor at a distance of 0.277 nm and three at a distance of 0.294, in average 0.290 nm. The mean distance between the nearest neighbors of the molecule is approximately 5.5 % greater than between the ice molecules. The other molecules are at distances which are intermediate between the first and second neighboring distances. The distance 0.41 nm is a distance between atoms O–H in an H_2O molecule.

The main differences between the structure of liquid water and the structure of ice are a more diffuse arrangement of the atoms in the lattice and a disturbance of the remote order. Heat fluctuations result in the bending and breakage of hydrogen bonds. Water molecules of the equilibrium positions get into neighboring voids of the structure and remain there for some time since these voids have the corresponding relative minimums of potential energy. This leads to an increase in the coordination number and to the formation of the lattice defects, whose presence determine

Fig. 2.4 Scheme of partial destruction and formation of hydrogen bonds at ice thawing (hopping time is 10–12 s.)



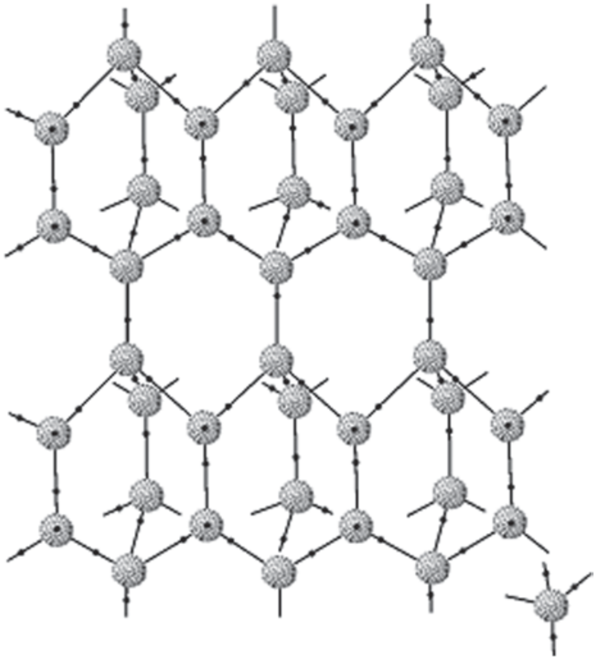


Fig. 2.5 Water as a pseudo-crystal

anomalous properties of water. The coordination number of molecules (the number of the nearest neighbors) varies from 4.4 at 1.5 °C to 4.9 at 83 °C.

Ice X Under the water pressure, magnified 600,000 times, water molecules snag so tightly against each other that the differences between hydrogen bridges and conventional chemical bonds completely disappear. Ice X possesses the greatest density among known crystalline forms of H_2O (2.51 g/cm^3). Its pressure remains hard even at a temperature of 500 °C.

In the gaseous state, water molecules cut loose from each other and embark on a solo voyage. Only occasionally do their individual elements join each other on the fly. Transforming into steam, water absorbs an enormous amount of energy—2,258 J/g (in comparison, with ethanol it is only 854 J/g). During condensation, this energy is liberated again. That is why water vapor may cause serious burns.

When and into what does water transform? To have a more graphic picture, these data is presented in the following form:

The state of the water under different conditions				
Temperature °C				
From −50 to +100	0	+4	+100	+374
In this temperature range at a pressure of 200 MPa, the running water splits into two structures of different density	This is the melting and freezing point. When freezing, the water "explosiveness" sharply increases all at once by 11 %	The water reaches it's the greatest density	This is water's boiling point under conditions of normal pressure. On Everest, for instance, due to low pressure, water starts to boil as early as 70 °C	Higher than this critical point and at a pressure of 22.1 MPa, the difference between the liquid and gaseous state of the water levels out. The matter then takes some intermediate form

Nearly all temperature scales have to do with water, including Kelvin's temperature scale which is based on the triple point of water, defined as exactly 273.163 K or 0.01 °C. It uses the same graduations as in Celsius's scale.

The above data give a graphic example of the anomalous behavior of water; for example, "abnormal" temperatures of water melting and boiling are shown. However, this is far from the only example of water abnormality. The reason for abnormal properties of water is the hydrogen bonding and peculiarities of water structure. The present cluster model of water (for details, see Chap. 3) explains many of its abnormal properties.

Thus, a hydrogen bridge (link) is a linking element, a normal, so-called, covalence link between one molecule and a normal link for the molecule of the weak Van der Waals attraction force. In a water drop the myriads of particles form an infinite network of tetrahedrons, while hydrogen bridges are organized into an ordered system. In doing so, they are flexible and compliant, which ensures variation of the water. The extreme lightness of ice is related to the fact that hydrogen bridges weave water molecules in a crystal into volumetric networks in such a way that much space remains between particles. During the melting phase, the regular network is partially broken and turns into liquid, which increases the density of the water.

The aforementioned phenomenon can be explained by discussing hydrogen bonds (bridges). The diversity of macroscopic solid forms of H_2O is reflected at the molecular level. The variants of the H_2O crystals demonstrate complexity and sophistication which cannot be compared with any other molecule. As has already been noted, 15 types of crystals are known. Christopher Zalzman from Oxford University announced the last two discoveries in March 2006. In paper [3], the summarized information about properties of all 15 types of water is presented. Thomas Lepting, from the Institute of General Inorganic and Theoretical Chemistry at the Innsbruck University, has been researching ice since 1980. "Even under normal pressure there are two forms of ice", he states. These are the so-called hexagonal and cubic ice, *Ih* and *Ic,* respectively. On Earth hexagonal ice is almost exclusively found. Snowflakes, ice covering lakes and ponds and ice cubes in a glass with a drink consist of this ice. Its particles form a hexagonal structure. The basic form of the other kind of ice is a cube. Such crystals which have a cubic shape can be found only at high altitudes of the earth's atmosphere, where deathly cold reigns. However, both variants of ice are united by one property—third-dimensionality.

It is not simple to account for possible types of crystalline varieties of ice. Water is also capable of forming glassy and amorphous forms. Scientists believe that 99.9 % of ice in space is in the amorphous form. It covers dust particles in interstellar space and is incorporated by comet composition.

The difference between crystalline and amorphous ice lies in their internal structures. In a crystal, water molecules are arranged in a regular way in all directions with identical interspaces. In the amorphous state they are chaotic, just as in the liquid state—as if the liquid had solidified instantaneously. The most well known representative of such form of matter can be found on an ordinary window pane.

According to one scientific interpretation, ice has become the basis of life on the Earth. Its flexible structure makes it possible to free such elements as nitrogen, oxygen and carbon. Upon interacting with each other, these substances form simple biomolecules. On Earth, universal vitrified ice may be obtained if over hundredth of a fraction of a second one is able to decrease the temperature by hundreds of degrees Celsius or in a high-pressure press. A piece of ice obtained in the Innsbruck Laboratory under the pressure 9.0 GPa at a sharp cool down is in fact amorphous ice—HAD (high-density amorphous ice). Externally, it does not differ at all from ordinary ice, but if it is thrown into a glass of water, it will sink because it is heavier than water. When heated, HAD is transformed into one more variant of vitrified ice, which, due to its low density, was referred to as LAD (low-density amorphous ice). However, when the scientists heated HAD in the press, having increased the temperature from 196 to +105 °C, the sample shrank. This contradicts the generally accepted idea that substances subjected to an increased temperature should expand. The scientists therefore stated that they had discovered the third variant of vitrified ice—very high-density amorphous ice (VHAD).

The state of the water when there is no difference between liquid and gas is achieved at the point with the temperature 374 °C and pressure 22.1 MPa. Scientists believe that at low temperatures such a point should also exist. Under experimental conditions, one manages to lower the water temperature to −38 °C, and in this case it does not freeze. Such phenomenon is seemed to be unreal however it does exist. Light clouds at an altitude of several kilometers above the Earth's surface form drops, and liquid remains at approximately the same temperature (−38 °C). When the temperature decreases, the "overcooled" water behaves in a more bizarre manner. Scientists imply that at a temperature of −50 to +100 °C and a pressure of 200 MPa the second critical point should be found (M. Chaplin, see [3] sticks to another viewpoint). Below this mark, in compliance with the theory, there are two varieties of liquid water with different densities; at a higher density, these variants are not distinguished.

It is assumed that two forms of ice, HAD and LAD, correspond namely to these liquid forms after their fast freezing processes. However, the result is that within one temperature range in which, despite all tricks of experimentalists, water drops

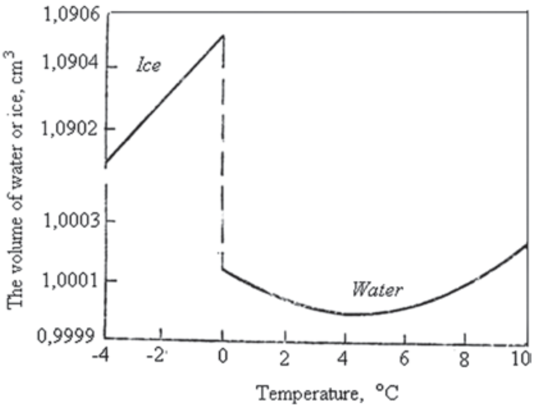


Fig. 2.6 Relationship between the specific volume of ice, water and temperature

always freeze. Should several forms of liquid water exist [1]? This is one of many questions for which there still no conclusive answer.

2.1.1 Anomalies of Water

It should be noted that anomalous properties of water, like anomalous properties of oxygen molecules, are important factors for the existence of the Earth's biosphere [4]. So, how many anomalies are present in water? Some scientists have counted 40 anomalies characteristic of water [1]. According to [3] there are 63 of them. These scientists have tried to explain such anomalous properties of water; to some they seem exhausting, to others they are controversial, and to the rest they are unsatisfactory.

How important the role of the anomalous properties of water in life is can be understood, for example, by considering its special properties at 4 °C (Fig. 2.6). For direct determination of the ice structure and liquid water, the data of the X-ray diffraction analysis and the scattering of slow neutrons are used [5–9]. In these methods, the main structural characteristic is the distribution function of the distance between the oxygen atoms. For water at 1.5 °C, the maximum of this function corresponds to the distance between the nearest water molecules in 0.290 nm, which slightly exceeds the distance between the molecules of the water in ice (0.276 nm). In this case, the average coordination number (n) of each water molecule equals 4.4. In other words, the destruction of hydrogen bonds in melting ice does not imply an increase in the density of liquid water, and the reason for this lies in a large coordination number of molecules. This is due to the fact that they partially occupy hollows, which are vacant in ice.

Close values of the distances between molecules of liquid water and ice as early as 1933 made it possible for a number of authors to express the opinion that water is a pseudocrystal [10] (Fig. 2.5). In turn, one author succeeded to qualitatively explain why water density at 4 °C reaches a maximum. Therefore, in accordance with

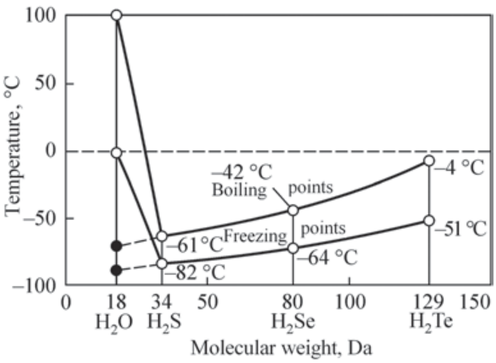


Fig. 2.7 Anomalies of boiling and freezing water points compared with other hydrogen compounds

this model, the water in the liquid state close to 0 °C represents a mixture of three components with various structures, which correspond to hexagonal ice, crystalline quartz and the densely packed structure of liquid water. As the temperature rises, ice-like structures are destroyed, and the contribution of the densely packed structure of the water increases. At $T > 4$ °C, the effect of increasing the distance between the molecules starts to prevail. It is determined by the heat caused by movement which leads to the decrease of water density. In the following years, several types of cluster models were developed. These models made it possible to explain the bulk of anomalies both of pure water and the water containing ions or molecules [11–16].

The maximum density of water at 4 °C, together with a low density of ice, result in that prior to freezing, it is necessary that the entire volume of fresh water (not only its surface) is close to 4 °C. Since the freezing of rivers, lakes and oceans moves from top to bottom, there is a possibility for the bottom ecosystem to survive, insolating the water from further freezing, reflecting the sunlight into space and thawing the water's surface.

Thanks to heat convection, which is controlled by density, seasonal mixing in deeper water of the moderate climate occurs, carrying life-supporting oxygen to its depths. The high heat capacity of oceans and seas makes it possible for them to act as heat reservoirs in such a way that marine temperatures vary only by one third. This is caused by the change of the land's temperature, which determines our climate (for example, the Gulf Stream carries tropical heat to north-western Europe).

Water compressibility decreases the level of the sea by approximately 40 m, which gives us 5 % more land. A high surface tension of water, plus its expansion when freezing, stimulates the erosion of stones, thus forming soil for agriculture.

The opposite properties of hot and cold water (see Fig. 2.7) are noted among its anomalies, which have already been mentioned in Sect. 2.1. These properties are expressed more vividly at lower temperatures, when the properties of the overcooled water deviate from hexagonal ice. If the water—oxygen hydride H_2O were a normal monomolecular compound, such as its analogies of the sixth group of D. I. Mendeleyev Periodic System of Elements, sulfur hydride H_2S, selenium hydride H_2Se, tellurium hydride H_2Te, then water in the liquid state would range from −90 to −70 °C. With such properties of water, life on Earth would not exist.

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