

PHYSICAL PROPERTIES OF WATER IN VARIOUS AGGREGATIVE STATES

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Summary

This chapter considers natural and chemical properties of water. The significance of different aggregative states of water for optimum conditions of life on the Earth is shown. Freezing and boiling of water, the irregular density, thermal capacity and solution power are explained, using the theory of water structure. The singularities of electrical and acoustic water properties are described. Modern representations on water viscosity are introduced. Statements are made on solar radiation absorption and diffusion in water bodies.

1. Common information

Water is a chemical compound which occurs in a liquid, solid and gaseous state. The aggregative state of water depends on the ratio of temperature and pressure. At a temperature of $\theta = 273.16$ K (0.00750°C) and pressure $p = 610$ Pa (4.6 mm of mercury) water can be in three aggregative states at the same time. This condition is marked by a triple point on the phase diagram. At any other natural combinations of θ and p water is in one of the three possible aggregative states. The equiprobable existence of water in a liquid and gaseous condition is declared by the curve of vaporization. The curve of

sublimation corresponds to temperature and pressure of ice and the water vapor equilibrium condition. The curve of melting divides the areas of water and ice.

1.1. Freezing

Water freezing is a complicated hydrophysical process. Hydrological aspects of the process are connected to seasonal peculiarities of ice cover formation, size of the water bodies, morphology of rivers, etc. Ice presence in water reflects a response of the water body to heat interaction between the water mass and the bounding environment (air, ground). In water bodies with an open system ice emerges in conditions of water mass supercooling. Usually water supercooling is stimulated by directed heat exchange with colder air in the autumn-winter season. Supercooling of a water body is a necessary, but an insufficient factor of ice formation. Crystal water can be in a liquid aggregative state at a temperature much lower 0 °C. Crystallization centers (nuclei) are an important factor of ice formation. They may be suspended sediments or small-sized crystals of ice. Crystals of ice are the usual forms of crystallization centers. The most probable zone of their origin is the thin surface water layer, where the temperature gradients are greatest. Strong water supercooling (down to –1.4 °C) is possible in a very thin surface water layer (0.6 to 6.0 mm), creating maximum probability of formation of ice crystals. The lower the water temperature and the faster the cooling of the water body, the more crystallization centers are formed in this layer, with smaller crystal size. Under conditions of supercooling of water, their linear size d_k rapidly increases. The intensity of this increase is close to the linear function of water supercooling. The third aspect of change of phase stability is rapid removal of latent heat of ice formation. If the removal of latent heat is slow or absent, the process of ice formation becomes slower and may cease.

The dissolved matter in water noticeably changes the freezing process. In particular it reduces temperature of freezing. The degree of its drop depends on water mineralization and the structure of the dissolved matter. Up to 5–6‰, temperature of water freezing is

$$\theta_s = -1.86Ci, \quad (1.1)$$

where 1.86 is the cryoscopic constant, C is the concentration of the dissolved matter in moles (ratio of amount of substance (g) in 1000 g of water to its molecular weight), I is isotonic coefficient. Its magnitude is

$$I = 1 + \alpha(k - 1) \quad (1.2)$$

Here α is the degree of the dissolved matter dissociation (that is the ratio of the amount of dissociated molecules to their total number in a solution), k is the number of ions originating at the molecules dissociation. The increase of water salinity reduces both the freezing-point and the maximum density. At water salinity less than 24.7‰ water freezes after it reaches its maximum density. Otherwise its density does not reach the maximum value. This influences the mixing process of water bodies during their autumn cooling.

The intensity of cooling depends on the type of water body. Rivers cool rather fast owing to the high intensity of mixing processes and the consequent uniformity of temperature distribution. Reservoirs cool down slower. Duration of cooling of a well-mixed water layer with thickness H from $\theta_1 = \theta$ up to $\theta_2 = 0$ °C at the intensity of heat loss from a square unit Q_t is

$$T = \frac{c\rho H\theta}{Q_t}. \quad (1.3)$$

1.2. Evaporation

Evaporation is the process of water conversion from liquid to gaseous state with rise in water temperature. At constant volume it is accompanied by an increase of steam pressure above an evaporating surface. Under natural conditions, pressure increases with the rise of evaporation rate, but for water bodies this relationship is essentially less significant in comparison with closed thermal systems. Evaporation reflects progressively the varying relation between kinetic energy of molecules, E_k , characterizing their capacity for greater or smaller deviation from an equilibrium state to potential energy E_p of molecular gravitation. At the surface layer potential energy is proportional to the work necessary for overcoming the forces of surface tension F_n . As E_k is approximately equal to zero, for individual or many molecules E_k is greater than F_n , and they have the possibility of overcoming the forces of surface tension and to convert to a gaseous state. The higher the water temperature, the greater the number of such molecules, and the faster their evaporation. The relationship between variables is non-linear, as the specific water heat (4200 Joule·kg⁻¹·K⁻¹) is anomalously high. Water has a very high value of heat necessary for conversion into vapor, in comparison with other fluids. It requires 2255.6 Joule to evaporate 1g of water at the boiling-point and normal atmospheric pressure.

The intensity of evaporation depends on velocity of vapor removal from a surface. In natural conditions this is closely related to wind velocity. The more wind velocity, the faster water evaporates. This phenomenon reflects (other conditions being equal) an acceleration of the process under increase of vertical gradient of water vapor concentration. Increased rates of evaporation under vapor removal from an evaporating surface also requires diminution of the alternate process—condensation. These two processes coexist in time. Condensation involves partial return of vapor to water bodies owing to the high elasticity of water vapor and thermobaric conditions favorable for change of phase. In some rare situations the intensity of evaporation and condensation can be equilibrated, and the total effect of both processes is close to zero.

1.3. Isotopic aspects

The molecule of water (H₂O) consists of atoms of hydrogen and oxygen. The existence of the three hydrogen (¹H – protium, ²H – deuterium (D), ³H – tritium (T)) and six oxygen (¹⁴O, ¹⁵O, ¹⁶O, ¹⁷O, ¹⁸O, ¹⁹O) isotopes indicates that generally water is a mixture of various isotopes. Each kind of isotope differs, according to the mass numbers of hydrogen and oxygen isotopes, in terms of their stability, and radioactive properties. In fluvial, lake, pluvial, melted, glacial, underground and marine water the most common

form of oxygen is the “easy” one, ^{16}O ; less common is the “heavy” isotope ^{18}O , the oxygen isotope with mass number 17 is very rare. The most common water isotope integrates protium and oxygen isotope ^{16}O . It forms 99.73% of the water resources of the planet (see Table 1). The other kinds of water comprise only 0.27% of this volume. Tritium waters (HTO) are only 13–20 kg in the entire Earth’s hydrosphere. In the atmosphere its amount is only about 0.07–0.10 kg. In the oceans its content is less than in continental waters. Each type of natural water has a specific isotope structure. Pluvial water is enriched by protium. Conversely, in melted water, the content of heavy isotopes of hydrogen is rather less, and concentration of oxygen isotopes ^{18}O is relatively high. The heavy water content in rivers and lakes has a deuterium to protium ratio of about 1:6800; in the Ocean it is 1:5600, and in Arctic ice it is 1:5500.

| Isotope type | $^1\text{H}_2^{16}\text{O}$ | $^1\text{H}_2^{17}\text{O}$ | $^1\text{H}_2^{18}\text{O}$ | $^1\text{HD}^{16}\text{O}$ | $^1\text{HD}^{18}\text{O}$ | D_2^{16}O |
|--------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|----------------------------|---------------------------|
| <i>N</i> , % | 99.74 | 0.04 | 0.20 | 0.0149 | 0.000057 | 0.00000023 |

Table 1. Content (*N*) of isotope varieties H_2O in natural waters

There are eighteen stable isotope types of water in nature. Theoretically their quantity is much greater. Heavy water occupies a special position. It has the ability to decelerate chemical reactions and some other anomalous properties.

1.4. Molecular structure

The mass number of a molecule $^1\text{H}_2^{16}\text{O}$ (hereinafter H_2O) is equal to 18. The weight ratio of atoms of these chemical elements is 2:16. Hydrogen forms 11.19% and oxygen 88.81% of the mass number of the water molecule. The nuclei of atoms in the molecule, in an equilibrium state, form an isosceles triangle with two protons at its base and an oxygen atom at an obtuse angle. The equilibrium state of the molecule is hypothetical and corresponds to the lack of oscillatory and rotary motions at $\theta = 0^\circ\text{K}$. The angle H-O-H and the internuclear distances H-H, O-H are functions of the aggregative state of water (see Table 2). They reach minimum and maximum values in vapor and ice. The diameter of the water molecule is equal to 2.76 angstroms ($1\text{A}^\circ - 10^{-10}\text{ m}$).

| Aggregative state of water | Distance H-H, A° | Distance H-O, A° | Angle H-O-H |
|----------------------------|--------------------------------|--------------------------------|-----------------|
| Vapor | 1.51 | 0.96 | $104^\circ 27'$ |
| Water | 1.53 | 0.97 | $104^\circ 40'$ |
| Ice | 1.62 | 0.99 | 109° |

Table 2. Influence of the aggregative state of water on internuclear characteristics of its molecule

In common conditions the water molecule performs oscillatory and rotary motions stipulated by interaction with other molecules, temperature changes etc. This leads to alteration of internuclear characteristics. New values of H-H and H-O are connected with modification of the positions of electrons in relation to the nuclei. The average square of electronic distance from the center of the molecule masses r_m^2 is equal to $5.1 \pm 0.7 \cdot 10^{-18}\text{ m}^2$ in an equilibrium state. In other conditions, co-ordinates of the molecules’ nuclei differ from their equilibrium ones, and this influences the magnitude of r_m^2 and

internuclear characteristics. Deviations of nuclei from their equilibrium position have an oscillatory character and can be described by superposition of a limited number of basic oscillations. Three basic types of oscillations (symmetrical or asymmetric oscillations of expansion and oscillation of curving) are distinctive for water.

The common energy of the water molecule is the difference between the molecular energy in an equilibrium state and the energy of electrons and nuclei being in quiescence on infinite removal from each other. Its value includes the kinetic energy of electrons, the Coulomb's potential energy and the potential energy of nuclei. The formation of the water molecule from two atoms of hydrogen and one atom of oxygen requires $2\ 248.9 \cdot 10^5$ Joule·mole⁻¹ of energy.

Energy modifications at the phase change are insignificant in comparison with energy consumption of electrons in a water molecule. Modification of the internal energy on phase change from liquid to vapor at $\theta = 100$ °C is equal to $4.04 \cdot 10^4$ Joule·mole⁻¹, and is compared to energy modifications of the water molecule during weak oscillations of the atoms' nuclei. Melting of ice causes mutation of this energy at $0.622 \cdot 10^4$ Joule·mole⁻¹.

Under equilibrium conditions combining hydrogen and oxygen atoms into one molecule is accompanied by enthalpy of their internal energy. This is equal to $-9.856 \cdot 10^5$ Joule·mole⁻¹ and is called energy of water molecule formation (*EFW*). At $\theta > 0$ °K the expenditure of internal energy for molecule formation will noticeably increase, as it is necessary to compensate for the energy of rotation and other types of atomic and molecular motion. At $\theta = 25$ °C the enthalpy of water formation is equal $-9.96 \cdot 10^5$ Joule·mole⁻¹. The energy of the O-H connection is equal to $1/2$ *EFW* ($4.928 \cdot 10^5$ Joule·mole⁻¹) owing to the symmetry of the water molecule in an equilibrium condition. Dissociation energy of this connection is $4.56 \cdot 10^5$ Joule·mole⁻¹.

The molecule of water has a dipole moment. Within the framework of the theory of molecular orbits, this is connected with the character of electron distribution in a molecule. There are two electrons with opposite directions of rotation in each orbit. Two nuclei of hydrogen and one of oxygen are enclosed by ten electrons. In a free atom of oxygen electrons are distributed between *s*- and *p*- orbits. Two from eight electrons in the oxygen atom are situated in a spherical *1s*-orbit and are strongly connected with the nucleus. This connection is weaker for electrons on the *2s*- and *2p_x*-orbits. Nevertheless, it is still rather strong. The last two electrons are arranged between *2p_y*- and *2p_z*-orbits. Electrons rotate on four spread orbits. The axes of two orbits are directed along O-H connections. The electrons of two other orbits do not participate in formation of chemical connections. These orbits lie in a plane perpendicular to the H-O-H one, intersecting it at the point of the oxygen atom. In this case, according to the calculations, the H-O-H angle in the water molecule should be 90°. Actually it exceeds 104° (see Table 2). This signifies the existence of other mechanisms of O-H connections (apart from the chemical connections). Such a mechanism is the compound (cross) of electrons of oxygen atom rotating on *2s* and *2p_x*-orbits. The effect lies in increase of electronic density owing to overlapping *2s* and *2p_x*-orbits. A compound of *2s* and *2p_x*-orbits results in formation of two poles of negative charge at a great distance from the hydrogen atom. Protons are responsible for two poles of positive electrical charges in the water molecule. Consequently the water molecule presents a specific electronic cloud. It

involves hydrogen connections, tetrahedral disposition of compounded molecular orbits, and the existence of a dipole moment.

A dipole moment is the product of a charge at a distance between its positive and negative points. It characterizes molecules where centers of gravity of positive and negative charges do not coincide. The dipole moment of the water molecule is connected with peculiarities of an electronic cloud—existence of two positive (in a zone of hydrogen atoms) and two negative (in a zone of oxygen atoms) poles of molecule charge. They arise on account of the compound of electrons on $2s$ and $2p_x$ -orbits, which is why the magnitude of a dipole moment DM does not depend on electrons of the other orbits owing to their symmetrical disposition around the oxygen nucleus. $DM = 1.86D$. The unit of a dipole moment D is equal to $3.33 \cdot 10^{-12}$ a coulomb-meter.

At close in dipole molecules their mutual gravitation happens. Gravitation of centers of positive and negative charges is more than their repulsion, as the distance between them is rather small. The mutual gravitation of H_2O molecules, caused by the dipole moment, brings it to a hydrogen connection. The strength of the hydrogen connection takes an intermediate place between chemical (energy of connection $4.184 \cdot 10^5$ Joule·mole⁻¹) and inter-molecular (energy of connection $2.092 \cdot 10^3$ Joule·mole⁻¹) interactions. The energy of the hydrogen connection varies from 8368 up to 33 472 Joule·mole⁻¹. In ice crystals it is equal to 18 828 Joule·mole⁻¹, which corresponds to rather weak, easily destroyed and restored connections between molecules. This reaches a maximum when the distance between molecules decreases.

The formation of the hydrogen connection is mainly connected to peculiarities of hydrogen atoms. They are characterized by a small (0.1 angstroms) atomic radius and the lack of internal electron orbits. Repulsion between adjacent molecules is absent in these conditions. Conversely, they can interact with the formation of the hydrogen connection. This arises on the issue of donor-acceptor interactions between atoms of hydrogen and oxygen. These interactions are caused by an undivided pair of electrons on $2p_y$ and $2p_z$ -orbits and the water molecule dipole. Electrons of electronegative atom of one molecule can come nearer to a proton of the other one and form a hydrogen connection. If this water molecule represents itself as the proton donor, it is lighter and accepts a proton, forming another hydrogen connection. The greater the dipole moment, the stronger the hydrogen connection is. Various fluids are notable for DM magnitude and the defining of hydrogen connection. Water has a resistant hydrogen connection. It almost ten times greater than other fluids. Basically it is proper to water in a solid and liquid aggregative state. This connection is practically absent in the gaseous aggregative state.

The singularities of the electronic cloud of the water molecule, its dipole moment and ability to organize hydrogen connections create 'water structure'—the relationships (relative position, displacement and interaction) between molecules. Bernal, Fauler and Samoilov produced ideas and data from spectroscopic investigations of water molecules in the solid state (ice crystals) that indicated a tetrahedral lattice. Each water molecule participates in hydrogen connections with four adjacent H_2O molecules. The number of molecules participating in formation of water structure (ice crystals), is named the coordination number (CN). The oxygen atom of a central molecule is equidistant (at a

distance of 2.76 \AA) from the adjacent four atoms of oxygen in the angles of a tetrahedron. A tetrahedral ice structure is explained by the specificity of distribution of electronic density in each interacting water molecule. It is similar to the crystalline lattice of the mineral tridymite, but the silicon atoms are replaced with oxygen.

Water molecules in the junctions of this lattice oscillate around their average position. Frequency of these oscillations is rather great, and the average time of oscillations is, conversely, rather small – $\tau_k = 2 \cdot 10^{-13} \text{ s}$. Water molecules also rotate and make transmitting transitions but with smaller frequency. At $0 \text{ }^\circ\text{C}$ water molecules make up to 10^5 re-orientations per second in ice crystals. Therefore, $\tau_n \approx 10^{-5} \text{ s}$ and $\tau_k \ll \tau_n$. For various time periods, t , larger or smaller τ_n and τ_k , the ice structure will reflect all or separate processes influencing its origin. At $t < \tau_k$ (an instantaneous structure) the crystalline lattice has an unregulated character, as some molecules do not take an equilibrium position. Such structure is named an *I*-structure. If $\tau_k < t < \tau_n$, the structure of ice has a more ordered character (oscillatory-average) and is named a *V*-structure. This structure is characterized by hardly fixed molecules' located in junctions of the crystalline lattice. The influence of rotary and transmitting motions of molecules on the ice structure is less obvious, as the time of its detection is less τ_n . For the time period $t > \tau_n$ it is possible to clarify all singularities of molecule orientations and to receive the most common representation about diffused-averaged ice structure or about *D*-structure. Each molecule in the ice crystalline lattice has time to pass through all possible transitions and reorientation for this time.

At $CN = 4$, with a large angle H-O-H in the water molecule, in a solid aggregative state (see Table 2) and tetrahedral connection of adjacent molecules, the ice has a tracery structure with a large number of hollows. The coefficient of space filling is equal to 0.34. Theoretically this can reach 0.74 with dense packing of molecules. Distance between appropriate oxygen atoms is reduced as temperature drops, corresponding to more dense packing of molecules in ice crystals and increase of the strength of hydrogen connections. With fall of temperature from 0 to $-60 \text{ }^\circ\text{C}$, the inter-molecular distance decreases by 0.18%, thereby influencing the physical properties of ice.

Temperature is not a unique reason for modification of structure and properties of ice. Pressure is also an important factor. For some combinations of temperature and pressure the existence of polymorphic ice is possible. Common ice (ice *I*) is formed with natural modifications of temperature and pressure. With high artificially-created pressure, it is possible to obtain 11 ice modifications, distinguished by mutual disposition of water molecules in ice crystals. Co-ordination number, inter-molecular distances and crystalline symmetry vary simultaneously and it causes, in particular, anomalous density of polymorphic types of ice.

From the start of ice melting and up to its completion, temperature rise does not cause the destruction of the tetrahedral lattice structure. While changing from the aggregative state into the liquid one, the structural characteristics of water undergo change: internuclear distances are decreased (see Table 2), and the co-ordination number and inter-molecular distances are increased (up to 2.9 \AA). If at $0 \text{ }^\circ\text{C}$ $CN = 4$, its appropriate values at 30 and $83 \text{ }^\circ\text{C}$ are equal to 4.6 and 4.9. The increase of CN is connected to the response of well-ordered and single water molecules with temperature rise. In a solid

state four adjacent molecules enclose the central water molecule. They are integrated by hydrogen connections. The intensity of oscillatory, rotary and transmitting motions of molecules in a crystalline lattice is insignificant. The rise of temperature causes greater intensity of these motions. Some of the hydrogen connections (no more than 15%) fail. Moving free molecules can appear in the vicinity of a central molecule. As a result of the statistical calculations it appears that CN increases and exceeds 4.

In water, as well as in ice crystals, the molecules pass through fast (temporary equilibrium positions) and slower (diffusion) displacements. The distinctive time period of the first type of molecule movement is a little less than τ_k for ice. The equilibrium positions and molecular orientations are established by local modification. At a temperature of 0 °C the molecule displaces from an equilibrium position once in 10^{-11} s, and the distinguished time is $\tau_n \approx 1 \cdot 10^{-11}$ s, that is essentially less than in a solid aggregative state. Differences between τ_k and τ_n are small in water. Therefore the V and D -structures of water (at high temperature) differ a little. The differences between them increase when temperature falls.

In a gaseous state, water doesn't have any structure, as the hydrogen connections between water molecules fail. Water at its boiling point maintains the structure, as 32.5% of the hydrogen connections are maintained. Interactions between vapor molecules depend on the forces influencing their spatial location.

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Biographical Sketch

Nikolay Ivanovich Alekseevskiy, Russian, was born in 1950 in the North Caucasus region. His parents were agricultural workers. In 1968 he graduated from special courses of the Teacher Institute in Stavropol and began work in the school as teacher of physical education. From 1969 to 1972 he was in the army. He graduated from the Moscow State University (MSU) in 1978 and obtained a Ph.D. “Channel processes in the mouth of rivers with big sediment runoff” from the Department of Geography in 1981. In 1994 he defended his doctor’s thesis “Formation and movement of river sediment”. Since 1981 he has been working in MSU as a scientist, assistant professor, and professor at the Faculty of Geography (Department of Hydrology). He is now Chief of the Department of Hydrology at the Faculty of Geography (MSU). He has been a full professor since 1995. The sphere of his scientific interests is the theory of channel processes, river sediment, physical, chemical and biological processes in water bodies, and problems of eco-hydrology and water quality. He has more than 110 scientific publications devoted to different aspects of his science area including some monographs: “Formation and movement of river sediment”, “Movement of sediment in different parts of the catchment and sea coast zone” (with A.E.Michinov), “Hydrology of Terek and Sulak river deltas (with V.N.Mikhailov, M.V.Mikhailova, A.U.Sidorchuk), “River sediments and channel processes” (with R.S. Chalov and others). A full professor of MSU, he teaches courses on “Hydrophilics”, “Hydraulics of water streams”, and “Problems of Hydrology”. He is in charge of post-graduate students: 3 masters have been defended under his supervision. He is married, with one daughter.