PHYSICAL PROPERTIES OF SEAWATER, INCLUDING ITS THREE PHASES

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Contents

Summary

This article offers a brief overview of physical properties of seawater including its three states—liquid phase, sea ice and vapor. The liquid medium is a single-phase thermodynamic system, which is characterized by the following physical state variables: mass, volume, pressure, temperature, and salinity. From the standpoint of meteorology, oceanography, and climatology, of greatest importance are the anomalous thermal properties of water—a surprisingly large amount of heat is required to change water temperature, and to cool or evaporate it.

The thermal conductivity, specific heat capacity, and evaporation heat of seawater differ little from the respective values for fresh water. The surprisingly high latent heat of evaporation, which plays an important role in the heat balance of the near-surface water layer and in the atmosphere, is little affected by the salinity.

A large body of data collected by water sample analyses in different parts of the World Ocean, confirm the homogeneity of the water salt composition, which means that the percentage of all major ions in seawater is the same wherever it has been sampled. The above reasoning also suggests that seawater should contain all the chemical elements existing in nature, even though they may have not been found yet. The presence of salts in seawater brings about a number of phenomena, such as diffusion, osmosis, a reduction of the freezing point, an increase in the boiling point, and a decrease in the aqueous tension.

A typical feature of sea ice thermal characteristics, such as specific heat capacity, fusion heat, and thermal expansion, is the significant difference between their values and those of the pure ice. This is because of the above-mentioned shift in the freezing point of the sea ice. The sea ice provides good natural protection of polar seas against further cooling.

1. Introduction

The temperature distribution is the most important oceanologic field. Temperature of the World Ocean exerts a large forcing on Earth climate and vital activity. It has been ascertained that some fish species feel temperature fluctuations with an accuracy of 0.03 ^{o}C. Temperature of seawater has an influence on sexual maturation of fish, and therefore on periods and areas of spawning, on incubation (approximately inversely proportional to temperature), on the survival of fish larvae (increasing with temperature), on growth of planktonic food resources for fish, on feeding activity, and on metabolism and growth of fish (reduced if temperature is greater then optimal). Large spasmodic temperature variations can lead to large-scale fish underfeeding and delayed growth.

The principal ocean forcing on the atmosphere are the supply of moisture by evaporation from the ocean surface (approximately 3 x 10^{20} g/year), and heat including latent heat in vapor (approximately 2 x 10^{23} cal/year), open heat of radiation and turbulent change of heat. Temperature of the World Ocean surface is the principal oceanologic field determining the weather on Earth. Prolonged temperature variations of oceanic temperature o just one to two degrees literally, in some regions of World Ocean, can lead to disastrous natural phenomena, including floods, and droughts on continents, e.g. the well known El-Nino phenomenon in the tropical part of the Pacific Ocean.

The gas dissolving process in the ocean depends directly on temperature. Ninety percent of the Earth’s carbon dioxide (CO_2) is dissolved in the World Ocean. The global rise of carbon dioxide in the atmosphere (greenhouse effect) may be partly a consequence of the global rise in temperature on Earth but it is not the reason for it. The temperature rise of the World Ocean has produced a discharge of CO_2 to the atmosphere greater than the anthropogenic discharge.

The World Ocean acts as a huge settling tank for nature. When flowing over the continental surface, water leaches salts from the rocks and carries them into the ocean. Therefore, in the process of its development, the World Ocean has been enriched and is still being enriched with salts. Large geological time intervals along with horizontal and vertical water movements have resulted in the World Ocean water being well mixed. The distribution of the main salt concentrations is now relatively uniform. A distinction needs to be drawn, however, between the major components of seawater salts, for which the law of uniformity of ionic composition holds with high accuracy, and microelements, the concentrations of which may undergo significant incidental variations as a result of biological processes..

The concentration of salt is equalized by turbulent diffusion which is several orders of magnitude stronger than molecular diffusion. However, molecular diffusion is of great importance for another phenomenon, osmosis (see Section 2.2).

Viscosity, and its dependence on temperature, are of great importance for the vital activity of plankton, because it is water viscosity that allows planktonic organisms to hover. As follows from the name (Greek, *planktos* – drifting, being carried), planktonic organisms have very weak means of independent motion. For its existence, plankton needs to be able to hover in water. If such an organism has a spherical form, it would sink in accordance with Stokes' Law. Particles with a more complex shape are described by a similar expression with the specific surface area equal to the ratio of the surface to volume used, instead of radius. The greater the specific surface, the greater the effect of viscosity and the lower the velocity of sinking. Horns, needles, edges, and other formations on the surface of planktonic organisms help plankton to hover in water.

The temperature of maximum density of water is higher than its freezing point at salinities below about 24.7‰. These temperatures become equal at 24.7‰; and at higher salinities, the temperature of maximum density is lower than the freezing point. This means that water *compaction* (in terms of density) or *compression* (in terms of specific volume) takes place. A layer of abrupt change in the vertical distribution of density in an ocean (the main pycnocline) leads to the existence of a zone of minimum sound speed, This is between the surface layer which has a higher speed of sound and deeper layers, where the speed of sound is also relatively high. The existence of such a layer means that an acoustic wave from a source lying within one of the high speed layers will spread laterally as in a wave guide.

The overall salinity of sea ice depends on various factors, such as seawater salinity and the place where ice forms, the rate of its formation, and its age. Measurements showed that after an abrupt drop in temperature down to –40 ^{o}C, newly formed ice had a salinity of 10.16‰, while after a temperature drop down to –16 ^{o}C, the ice salinity was as low as 5.64‰. The salinity of ice decreases with its age, because the salt solution, which remains between the crystals during their freezing, is denser than the ice and therefore leaches down. The result is that by the late summer, the top ice layer in the Arctic Basin becomes fresh enough to be suitable for making drinking water.

In addition to the temperature, salinity, and pressure, one more physical characteristic of the sea ice is its porosity. The porosity stems from the large amounts of air that enter the ice after the brine has leaked down. This effect accounts for the ice of slightly salt seas containing less air than the ice of strongly salt seas. The sea ice of the slightly salt Gulf of Finland contains less than 4% of air, while in the strongly salt Barents Sea the ice air content can reach 8%.

2. Liquid phase

Liquid medium is a *single-phase* thermodynamic system, which can be characterized by the following physical state variables: mass, volume, pressure, temperature, and salinity. Of these variables, the first three are mechanical, the temperature is a thermodynamic variable, while the salinity, and the electric conductivity coupled with it, are physicochemical variables.
In oceanography, specific gravity and density along with the specific volume—an inverse variable with respect to density—are used instead of mass and volume.

2.1. Temperature

Water temperature in the seas is measured in degrees Celsius. The standard accuracy of temperature measurements is ± 0.01 ^{o}C. Temperature in oceans varies from –1.9 ^{o}C to ~ 30 ^{o}C. The lower boundary is fixed by ice formation. However, supercooled water can be met, which has temperature below the freezing point. Water temperature in the surface layer of a closed sea can be higher than 30 ^{o}C, but, such values have never been recorded in the open ocean outside a shelf zone.

Water is the most widespread mineral, and a number of properties suggest that the formula H_2O fails to adequately describe the molecule of water. Molecules of H_2O are polymerized by various chemical bonds so that their mean molecular weight is far greater than 18.

The melting and boiling points of some other substances with molecular weight close to 18 (see Table 1) are well below those of water; this can be attributable to their molecules not being polymerized.

Substance	**Formula**	**Molecular weight**	**Boiling point, ^{0}C**	**Melting point, ^{0}C**
Water	H_2O	18	100	0
Ammonia	NH_3	17.03	33.35	-77.7
Methane	CH_4	16.04	-161.49	-182.48
Hydrogen fluoride	HF	20.01	19.54	-83.1

Table 1. Boiling and melting points of water and some other substances with similar molecular weight

From the standpoint of meteorology, oceanography, and climatology, of greatest importance are the anomalous thermal properties of water—a surprisingly large amount of energy is required to change water temperature, and to cool or evaporate it.

The wide occurrence of water on the Earth is essential for life on the planet. The high heat capacity of water smoothes the difference in the extent of heating by the Sun between different areas on the land surface. Were the amount or the heat capacity of water not so large, the tropical zone would be much hotter and the polar zone much colder than they are now.

The root of all these anomalies lies in the structure of the water molecule. The point is that the hydrogen atoms in the H_2O molecule are not aligned with the central oxygen atom, but form an angle of 105 - 110^o. Because of this asymmetry, the water molecule forms a dipole with a dipole moment of 1.84×10^{-18}. As a result, H_2O molecules associate to form numerous complexes consisting of 2 to 8 molecules. Such complex loses their mobility and acquire the features of a high-molecular compound.

The high dipole moment at a relatively small molecular volume of water is the cause of its especially high dielectric constant: 80. Direct chemical consequences of this fact are the high ionizing power of water, i.e. its capability to split the molecules of dissolved substances into ions, and its ability to dissolve other substances, which it demonstrates with respect to most inorganic chemicals.

Few compounds are known to have dielectric constant as high as that: e.g. NH_3 (23DK), HF (84DK), HCN (95DK), SO_2 (13.8DK). All these form the group of "water-like solvents". A specific feature of these solvents is their high capacity to form compounds with dissolved substances. In the case of water, this capacity manifests itself in the formation of hydrates and effects of neutralization and hydrolysis. A typical feature of such solvents is their weak ionization and low electric conductance when pure and a pronounced electric conductance in the form of solutions.

A column of pure water 1 mm in length at 18 ^{o}C has the same electric resistance as a copper wire with the same cross section and a length of 16×10^6 km (400 times the Earth's equator) or a column of seawater with a salinity of 35‰ and a length of 1–3 km.

The valence angle of about 110^o results in water molecules, in addition to their usual distribution in space, being able to combine to form tetrahedral structures. In liquid water, this brings about the formation of a temperature-dependent mixture of eight-, four-, and two-member molecules with a residue of single molecules. The two- and four-member molecules form linear chains, while the eight-member molecules form closed structures in the form of double tetrahedrons. The hollow internal space makes the volume of such molecules relatively large. These tridymite-like molecules are called "ice-forming", because they serve as a basis for the formation of the coarse-cellular lattice of ordinary ice. Such eight-member molecules occupy a volume 10% larger than the dense packing of spheres. The number of eight-member molecules increases with decreasing temperature.

As water gets cooler, two simultaneous processes proceed in it—a decrease in the volume because of cooling and an increase in the volume owing to the formation of the eight-member molecules. These processes reach equilibrium at 4 ^{o}C, when water has maximum density. As the temperature decreases from 4 ^{o}C to 0 ^{o}C, the processes of thermal expansion become predominate until 0 ^{o}C, when water freezes and all the molecules aggregate to form tridymite-like crystal lattices with hydrogen bonds. This mechanism is responsible for a 9% jump-like increase in the volume when water turns into ice.

This provides an explanation for the oceanographically important fact that water is heavier than ice. Only a few substances, e.g. bismuth, gallium, germanium, stibium, silicium, and some organic liquids that form liquid crystals, are known to have the anomalous property of their solid form being less dense than the liquid form.

A consequence of water expansion at freezing is the considerable pressure that ice can exert on solid walls that constrain it. Such pressure can be as large as 2100 kg/cm^2 at –22 ^{o}C, and it is of paramount importance in rock destruction under natural conditions. Figure 1 gives the water state diagram (according to Bridgeman). At a pressure above 2100 kg/cm^2, the anomalous ice, which is lighter than water, transforms into other forms of ice, i.e. II, III, V, and VI types. As opposed to type I, these types are normal, i.e. they are more dense then the liquid media in equilibrium with them.

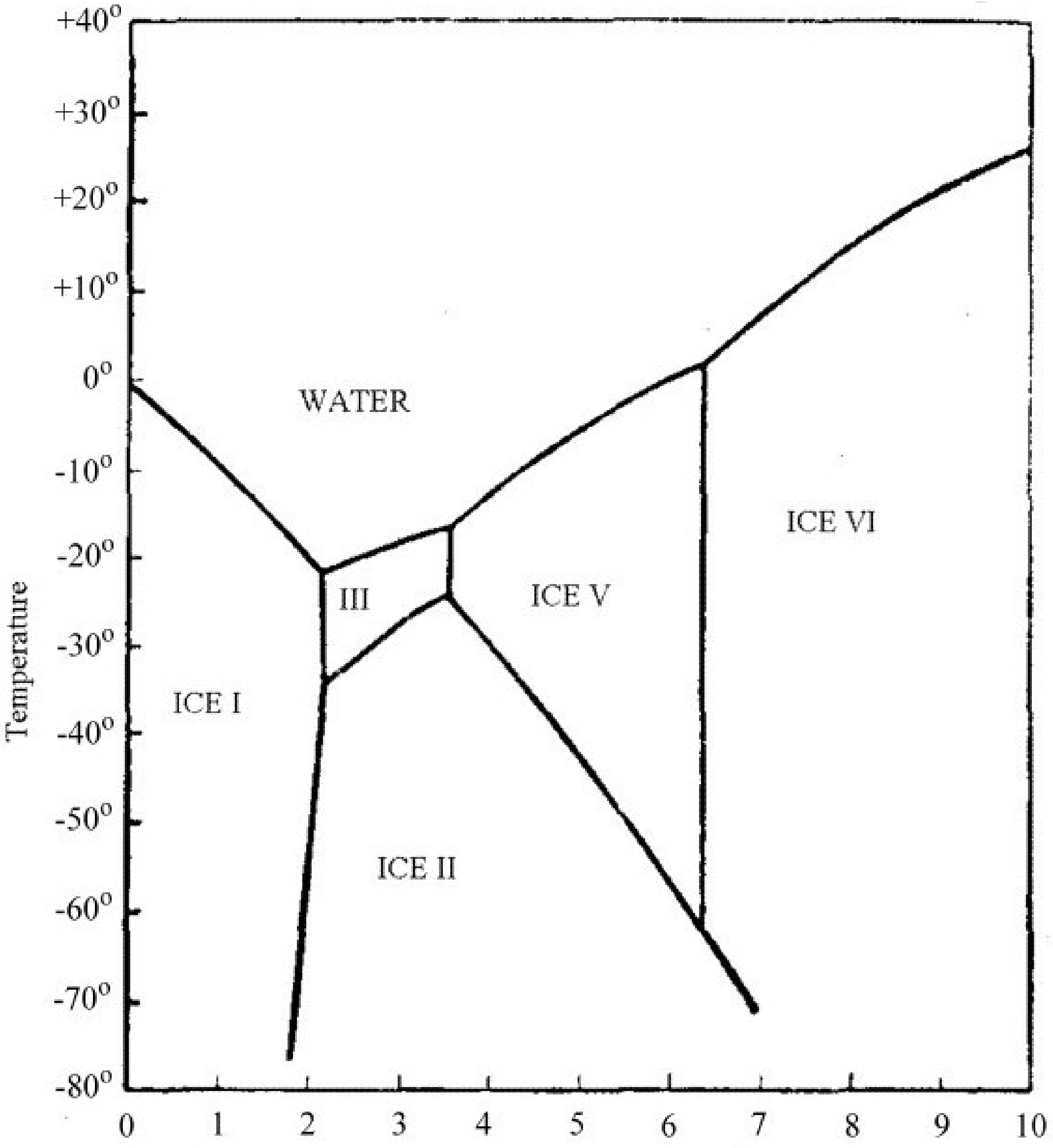

Figure 1. Water state diagram (according to Bridgeman)

Changes in temperature have the following effect on freshwater properties:

- ***a decrease in temperature reduces*** water density, index of refraction, and surface tension;
- ***a decrease in temperature causes an increase*** in specific heat capacity, compressibility (which causes an anomalous drop in the sound speed), the diluting capacity, and viscosity;
- ***intermediate minimums appear*** in the density at 4^0C and in the index of refraction at -1 ^{o}C;
- ***intermediate maximums appear*** in specific heat capacity at 34 ^{o}C, compressibility at 40 ^{o}C, oxygen solubility at 80 ^{o}C, and hydrogen solubility at 37 ^{o}C.

Water has a heterogeneous composition and its molecule can exist in 9 isotopic forms. Hydrogen has three isotopes ^1H (protium) with a mass of 1, ^2H (deuterium) with a mass of 2 and tritium ^3H with a mass of 3. Deuterium is denoted by D. Oxygen has six isotopes ^{14}O, ^{15}O, ^{16}O, ^{17}O, ^{18}O and ^{19}O. Combinations of the first two hydrogen isotopes with three oxygen isotopes with the atomic weights of 16, 17, and 18 yield nine water types: $^1H_2{}^{16}O$ (99.73%), $^1H_2{}^{18}O$ (0.2%), $^1H_2{}^{17}O$ (0.04%), $^1H\,^2H\,^{16}O$ (0.032%), $^1H\,^2H\,^{18}O$ (0.00006%), $^1H\,^2H\,^{17}O$ (10^{-5} %), $^2H\,^{16}O$ (3 x 10^{-6} %), $^2H_2\,^{18}O$ (6 x 10^{-9} %), and $^2H_2\,^{17}O$ (10^{-9}%). Figures in parentheses are the percentages of the respective types in natural water.

Physical characteristics	**Natural water**	**Deuterium oxide (heavy water)**
Density at 20 ^{o}C	0.99823	1.1051
Density peak at	4 ^{o}C	11.6 ^{o}C
Melting point	0 ^{o}C	3.80 ^{o}C
Boiling point	100 ^{o}C	101.42 ^{o}C
Dynamic viscosity at 20 ^{o}C	0.01002 g/(cm · s)	0.0126 g/(cm · s)
Surface tension at 20 ^{o}C	72.53 dyn/cm	67.8 dyn/cm

Table 2. Properties of natural (ordinary) and heavy waters

The term *heavy water* means deuterium oxide $^2H_2\,^{16}O$ (D_2O); its physical properties differ significantly from those of ordinary water. Of great importance is the difference between steam tension values for different water components. Thus, the steam tension of heavy water D_2O and water $^1H\,^{18}O$ at 20 ^{o}C are 7.2% and 0.94% lower than that of ordinary water. Therefore, evaporation is accompanied by partial fractionation of the water mixture. Samples of water of different origin exhibit notable differences. Water in plants and minerals is heavier, whereas water in living organisms is lighter than the oceanic water.

2.1.1 The thermal conductivity, specific heat capacity, and evaporation heat

The thermal conductivity, specific heat capacity, and evaporation heat of seawater differ little from the respective values for freshwater. The thermal conductivities of freshwater (0 ‰) and seawater (40 ‰) at 17.5 ^{o}C are 1.40 x10^{-3} and 1.34x10^{-3} cal cm^{-1} grad^{-1} s^{-1} respectively.

The specific heat capacity of seawater at constant pressure C_P decreases with increasing salinity, temperature, and pressure. Oceanic water with a salinity of 34.85‰ contains about 7% less heat than the same amount of freshwater. The value of C_P varies from 1.0 at zero temperature at the surface to 0.884 at salinity of 34.85‰ and pressure of 10 000 decibar. The specific heat capacity at constant pressure C_v is less than C_P by no more than 2%, so that the ratio C_P / C_v for seawater at 34.85‰ salinity and 0 °C equals γ = 1.0004; whereas at 30 °C, γ = 1.0207. The ratio γ is of great importance for evaluating sound speed (see section 2.4).

The surprisingly high latent heat of evaporation, which plays an important role in the heat balance of the near-surface water layer and in the atmosphere, is little affected by the salinity. Evaporation of 1 g water at 0 °C requires 597 cal.

When rising into layers with lower pressure, water expands. By producing work against the external pressure, water decreases its temperature. A similar process, although in the opposite direction, takes place when water moves downward, provided no essential transfer of heat takes place. Such change in the temperature is referred to as adiabatic. The adiabatic change in temperature can be evaluated through Kelvin's formula, $dt = 10^5 \dfrac{geT}{Jc_P}$, where g is gravity acceleration; *J* is mechanical equivalent of heat; *e* is thermal-expansion coefficient; *T* is temperature, K; C_P is specific heat at constant pressure. For water at 0 °C and a salinity of 35‰, this characteristic equals 0.0035 °C per 100 m. The adiabatic temperature gradient in the lower atmosphere is about 300 times as large as that. For practical purposes, the measured temperatures are converted to the normal pressure. With this in view, the notion of potential temperature is introduced, i.e. the temperature that a water mass will attain after adiabatically rising to the surface $t_p = t_m - \Delta t_{ad}$, where t_m is the temperature measured at the relevant depth and Δt_{ad} is an adiabatic correction. The values of Δt_a were tabulated by B. Helland-Hanzen, who also coined the term “potential temperature”. A temperature t_m = 2.48 °C at a depth of 10 000 m corresponds to t_p = 1.17 ^{O}C, which yields Δt_{ad} = 1.31 ^{O}C. The potential temperature is used in the following cases: when temperature is used to study the spreading of water masses in the World Ocean; when there is a need to assess the depth of a threshold separating two sea basins; when the stability of water mass needs to be estimated. The increase in temperature, recorded in the near-bottom horizons of many seas, should be attributed largely to the adiabatic rise in temperature rather than heat inflow from the deeper Earth layers.

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Biographical Sketch

Valery N. Zyryanov is the head of the laboratory of hydrodynamics in the Water Problems Institute of the Russian Academy of Sciences, and Professor of Physics of Atmosphere and Hydrosphere. His monograph “The Steady Ocean Current Theory” (1985, Leningrad, Gidrometeoizdat) presents the mathematical fundamentals of the steady ocean current theory with consideration of bottom relief. The theory of ocean currents over ridges, seamounts and around islands is described. His monograph “Topographic Eddies in Sea Current Dynamics” (1995, Moscow) expounds results of theoretical and experimental studies of the dynamics of eddies above seamounts in oceans and seas. He continues working in geophysical hydrodynamics and applied mathematics, and lectures in the Faculty of Physics of M.V. Lomonosov Moscow State University.