

# WATER, PROPERTIES

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## Introduction

Our planet is the planet of life primarily because it is blessed with the precise ranges of temperature and pressure that make possible the existence in a liquid state of a singular substance called water. So ubiquitous is water on our globe, covering nearly three-quarters of its surface, that the entire planet really should be called ‘Water’ rather than ‘Earth.’ However, as Coleridge’s *Ancient Mariner* complained, most of the water everywhere is unfit to drink. Less than 1% of the water on earth is ‘fresh’ (i.e., non-saline) water, and that amount is unevenly distributed. Humid regions are endowed with an abundance of it, even with a surfeit, so that often the problem is how to dispose of excess water. Arid and semiarid regions, on the other hand, are afflicted with a chronic shortage.

Life as we know it began in an aquatic medium and water is still the principal constituent of living organisms. It is, literally, the essence of life. As Vladimir Vernadsky wrote a century ago: “Life is animated water.” Though we appear to be solid, we are really liquid bodies, similar to gelatin, which also seems solid but is in fact largely water, made consistent by the presence of organic material. The analogous material in our bodies is protoplasm. The water content of a newborn infant is nearly 90% water by mass, and even in adults it is over 65%. Actively growing herbaceous plants typically contain over 90% water. Far from being a bland, inert liquid, water is a highly reactive substance, a solvent and a transporter of numerous substances.

The importance of water was recognized early in history, yet little was known about its real nature. In the Middle Ages, people believed that fresh water emanated magically from the bowels of the earth. They could not imagine that all the water flowing in innumerable springs and mighty rivers (such as the Nile, which appeared to the ancient Egyptians to come out of the driest desert!) could possibly result from so seemingly feeble a source as rain and snow. The first to conjecture this was Leonardo da Vinci, but only in the latter part of the seventeenth century did the English astronomer Edmond Halley and, separately, the Frenchman Claude Perrault prove the principle by calculation and measurement. Water was long thought to be a

single element, until early in the eighteenth century, when it was found to consist of hydrogen and oxygen in combination.

Notwithstanding its ubiquity, water remains something of an enigma, possessing unusual and anomalous attributes. Perhaps the first anomaly is that, being a compound of two gases and having relatively low molecular weight, water is a liquid and not a gas at normal temperatures. (Its sister compound, hydrogen sulfide,  $\text{H}_2\text{S}$ , has a boiling-point temperature of  $-60.7^\circ\text{C}$ .) Compared with other common liquids, water has unusually high melting and boiling points, heats of fusion and vaporization, specific heat, dielectric constant, viscosity, and surface tension.

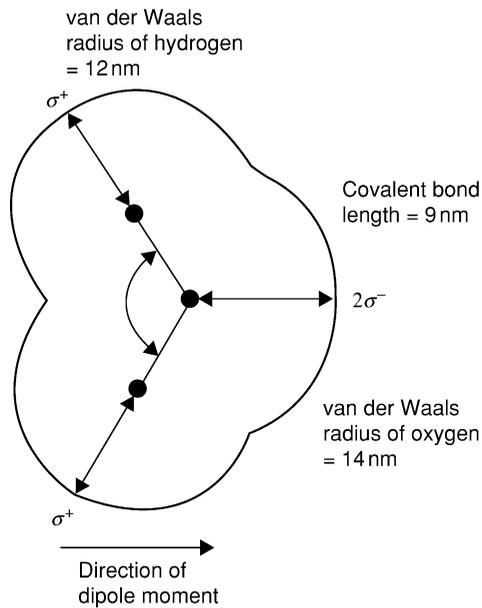
## Molecular Structure

One cubic meter of liquid water at  $20^\circ\text{C}$  contains about  $3.4 \times 10^{28}$  (34 billion billion billion) molecules, the diameter of which is about  $3 \times 10^{-10}$  meter ( $3 \times 10^{-4}$   $\mu\text{m}$ , or about 3 Angstrom units). The chemical formula of water is  $\text{H}_2\text{O}$ , which signifies that each molecule consists of two atoms of hydrogen and one of oxygen. There are three isotopes of hydrogen ( $^1\text{H}$ ,  $^2\text{H}$ ,  $^3\text{H}$ ) and three of oxygen ( $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ), which can form 18 combinations. However, all isotopes but  $^1\text{H}$  and  $^{16}\text{O}$  are quite rare.

The hydrogen atom consists of a positively charged proton and a negatively charged electron. The oxygen atom consists of a nucleus having a positive charge of eight protons, surrounded by eight electrons, of which six are in the outer shell. Since the outer electron shell of hydrogen lacks one electron and that of oxygen lacks two electrons, one atom of oxygen can combine with two atoms of hydrogen in an electron-sharing molecule.

The strong intermolecular forces in liquid water are caused by the electrical polarity of the water molecule, which in turn is a consequence of the arrangement of electrons in its oxygen and hydrogen atoms ([Figure 1](#)). The oxygen atom shares a pair of electrons with each of the two hydrogen atoms, through overlap of the 1s orbitals of the hydrogen atoms with two hybridized  $\text{sp}^3$  orbitals of the oxygen atom. The H–O–H bond in water is not linear but bent



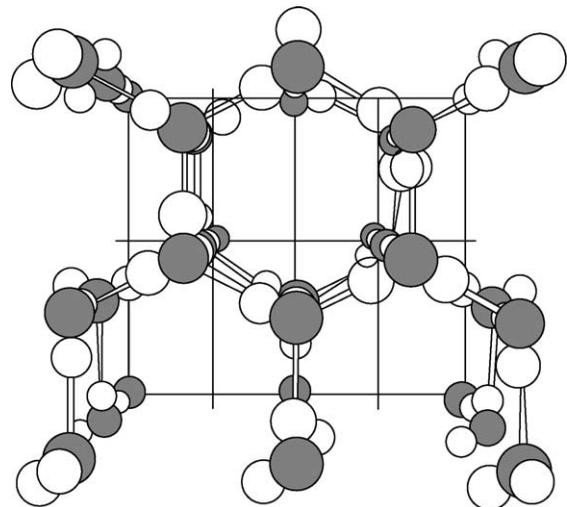


**Figure 1** Model of a water molecule. The curved lines represent the borders at which van der Waals attractions are counterbalanced by repulsive forces. Reprinted from *Environmental Soil Physics*, Hillel D (ed.). Copyright (1998), with permission from Elsevier.

at an angle of  $104.5^\circ$ . That angle deviates slightly from a perfectly tetrahedral arrangement of the oxygen atom's four possible  $sp^3$  orbitals, which would have an angle of  $109.5^\circ$ . The mean H-O interatomic distance is  $9.65 \times 10^{-5} \mu\text{m}$ . The arrangement of electrons in the molecule gives it electrical asymmetry. The electronegative oxygen atom tends to attract the single electrons of the hydrogen atoms, leaving the hydrogen nuclei bare. Hence, each of the two hydrogen atoms has a local partial positive charge. The oxygen atom, in turn, has a partial negative charge, located in the zone of the unshared orbitals. Thus, though the water molecule has no net charge, it forms an electrical dipole.

## Hydrogen Bonding

Every hydrogen proton, while attached primarily to a particular molecule, is also attracted to the oxygen of the neighboring molecule, with which it forms a secondary link known as a hydrogen bond. Though the intermolecular link resulting from dipole attraction is not as strong as the primary link of the hydrogen to the oxygen of its own molecule, water can be regarded as a polymer of hydrogen-bonded molecules. This structure is most complete in ice crystals, in which each molecule is linked to four neighbors via four hydrogen bonds, thus forming a hexagonal lattice with a rather open structure (Figure 2). When the ice melts, this rigid structure collapses partially, so additional molecules can



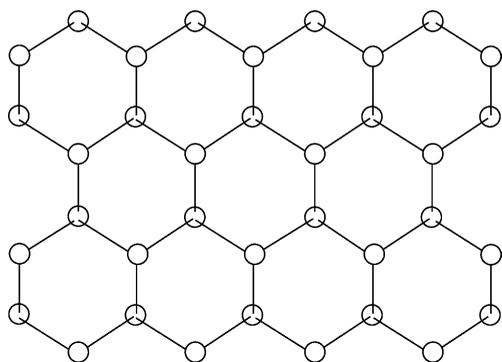
**Figure 2** Schematic structure of an ice crystal. The oxygen atoms are shown in gray and the hydrogen atoms in white. The pegs linking adjacent molecules represent hydrogen bonds. Reprinted from *Environmental Soil Physics*, Hillel D (ed.). Copyright (1998), with permission from Elsevier.

enter the intermolecular spaces and each molecule can have more than four near neighbors. For this reason, liquid water can be more dense than ice at the same temperature, and thus lakes and ponds develop a surface ice sheet in winter rather than freeze solid from bottom to top as they would if ice were denser than liquid water.

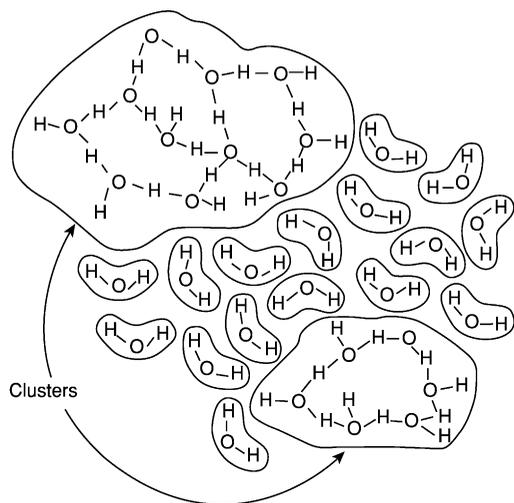
## States of Water

In the vapor or gaseous state, water molecules are largely independent of one another and occur mostly as monomers signified as  $(\text{H}_2\text{O})_1$ . Occasionally, colliding molecules may fuse to form dimers  $(\text{H}_2\text{O})_2$  or even trimers,  $(\text{H}_2\text{O})_3$ , but such combinations are rare. However, in the solid state a rigidly structured lattice forms with a tetrahedral configuration (Figure 2) that can be schematically depicted as sheets of puckered hexagonal rings (Figure 3). As many as nine alternative ice forms can occur when water freezes, depending on prevailing temperature and pressure conditions. Figure 3 pertains to ice 1, the familiar form, which occurs and is stable at ordinary atmospheric pressure.

The orderly structure of ice does not totally disappear in the liquid state. The polarity and hydrogen bonds continue to bind water molecules together, though the structural forms that develop in the liquid state are much more flexible and transient than in the rigidly structured solid state. Hydrogen bonds in liquid water form an extensive three-dimensional network, the detailed features of which appear to be short-lived. According to the 'flickering cluster' model discovered by Frank and Wen and modified



**Figure 3** The crystalline structure of ice. Reprinted from *Environmental Soil Physics*, Hillel D (ed.). Copyright (1998), with permission from Elsevier.



**Figure 4** Schematic illustration of 'flickering clusters,' showing polymeric associations and monomeric molecules in liquid water. Reprinted from *Environmental Soil Physics*, Hillel D (ed.). Copyright (1998), with permission from Elsevier.

by Erland, the molecules of liquid water associate and dissociate repeatedly in transitory or flickering polymer groups, designated  $(\text{H}_2\text{O})_n$ , having a quasi-crystalline internal structure. These microcrystals, as it were, form and melt so rapidly on the scale of picoseconds and randomly that, on a macroscopic scale, water appears to behave as a homogeneous liquid (Figure 4).

In transition from solid to liquid, and from liquid to gas, hydrogen bonds must be broken (while in freezing and condensation they are re-established). Hence relatively high temperatures and energies are required to achieve these transitions. To thaw 1 kg of ice,  $3.35 \times 10^5 \text{ J}$  ( $80 \text{ cal g}^{-1}$ ) must be supplied. Conversely, the same energy (the latent heat of fusion) is released in freezing. At the boiling point ( $100^\circ\text{C}$  at atmospheric pressure), water passes from the liquid to the gaseous state and in so doing it absorbs  $2.26 \times 10^6 \text{ J kg}^{-1}$  ( $540 \text{ cal g}^{-1}$ ). This

amount of heat is known as the latent heat of vaporization. Water can be vaporized at temperatures below  $100^\circ\text{C}$ , but such vaporization requires greater heat or lower atmospheric pressure. At  $30^\circ\text{C}$ , the latent heat is about  $2.43 \times 10^6 \text{ J kg}^{-1}$  ( $580 \text{ cal g}^{-1}$ ). Sublimation is the direct transition from the solid state to vapor, and the heat absorbed by it is equal to the sum of the latent heats of fusion and of vaporization.

## Ionization and pH

Because of its small mass and the tightness with which its single electron is bound to the oxygen atom, the nucleus of the hydrogen atom in the water molecule exhibits a finite tendency to dissociate from the oxygen with which it is covalently associated and to 'jump' to the adjacent water molecule, to which it is hydrogen-bonded. Such an event produces two ions: the hydronium ion ( $\text{H}_3\text{O}^+$ ) and the hydroxyl ion ( $\text{OH}^-$ ). The reaction described is reversible, and should be written as:



However, by convention it is written simply as:



and one speaks of 'hydrogen ions' rather than of 'hydronium ions.'

Although the self-ionization of water is small, its consequences are extremely important. The ionization is reversible, and it tends to an equilibrium state in which the rate of dissociation into ions equals the rate of ion reassociation to form molecules once again. For such a system in equilibrium (at which the concentration of each of the species  $\text{H}_2\text{O}$ ,  $\text{H}^+$ , and  $\text{OH}^-$  remains constant), the law of mass action applies; i.e., the ratio of concentrations of the products and the reactants must be constant. Using brackets to denote concentration, we can write this in the following way:

$$K_{\text{equil}} = [\text{H}^+][\text{OH}^-]/[\text{H}_2\text{O}] \quad [1]$$

Since the number of water molecules undergoing dissociation at any given time is very small relative to the total number of water molecules present,  $[\text{H}_2\text{O}]$  can be considered constant. Assuming this concentration to be  $55.5 \text{ mol l}^{-1}$  (the number of grams per liter divided by the gram molecular weight:  $1000/18 = 55.5 \text{ mol l}^{-1}$ ), we can simplify the equilibrium constant expression as follows:

$$55.5 \times K_{\text{equil}} = [\text{H}^+][\text{OH}^-], \text{ or } K_w = [\text{H}^+][\text{OH}^-] \quad [2]$$

in which  $K_w$  is a composite constant called the ion product of water. In fact, the concentrations of  $H^+$  and  $OH^-$  ions in pure water at  $25^\circ C$  are  $10^{-7} \text{ mol l}^{-1}$ , an extremely small value when compared to the overall concentrations of (largely undissociated) water, namely  $55.5 \text{ mol l}^{-1}$ . Thus,  $K_w$  at  $25^\circ C$  is  $10^{-14}$ . If the hydroxyl ion concentration  $[OH^-]$  is changed, the hydrogen ion concentration  $[H^+]$  changes automatically to maintain the constancy of the product, and vice versa. An excess concentration of hydrogen ions over the concentration of hydroxyl ions imparts to the aqueous medium the property of acidity, whereas a predominance of hydroxyl ions produces the opposite property of alkalinity or basicity. A condition in which the concentrations of  $H^+$  and  $OH^-$  are equal is called neutrality.

The ion product of water,  $K_w$ , is the basis for the pH scale, a measure of the concentration of  $H^+$  (and of  $OH^-$  as well) in any aqueous solution in the range of concentration between  $1.0 \text{ mol l}^{-1} H^+$  and  $1.0 \text{ mol l}^{-1} OH^-$ . The pH is defined as

$$\text{pH} = \log_{10} 1/[H^+] = -\log_{10}[H^+] \quad [3]$$

As already stated, in a precisely neutral solution at  $25^\circ C$ ,

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ mol l}^{-1}$$

The pH of such a solution is

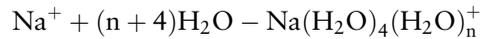
$$\text{pH} = \log_{10}[1/(1 \times 10^{-7})] = 7.0$$

The pH value of 7.0 for a neutral solution is thus not arbitrary, but derives from the value of the ion product of water at  $25^\circ C$ . The pH scale is logarithmic, not arithmetic. If two solutions differ in pH by one unit, then one solution has 10 times the hydrogen ion concentration of the other. Thus, a pH of 6 implies a hydrogen ion concentration of  $10^{-6}$  and a hydroxyl ion concentration of  $10^{-8}$ . A pH of 5 indicates  $[H^+] = 10^{-5}$  (acidity 10 times that of the above) and  $[OH^-] = 10^{-9}$ .

### Solvent Properties of Water

Water dissolves or disperses many substances because of its polar nature. Hence it has been called the universal solvent. All chemical substances have finite solubilities in water, but these solubilities range widely. Many crystalline salts and other ionic compounds readily dissolve in water but are nearly insoluble in nonpolar liquids such as chloroform or benzene. Since the crystal lattice of salts, such as sodium chloride, is held together by very strong electrostatic attractions between alternating positive and negative ions, considerable energy

is required to pull these ions away from one another. However, water dissolves sodium chloride because the strong electrostatic attraction between water dipoles and the  $Na^+$  and  $Cl^-$  ions, forming stable hydrated  $Na^+$  and  $Cl^-$  ions, exceeds the attraction of these ions to each other. In the case of  $Na^+$ , hydration is represented by the process:

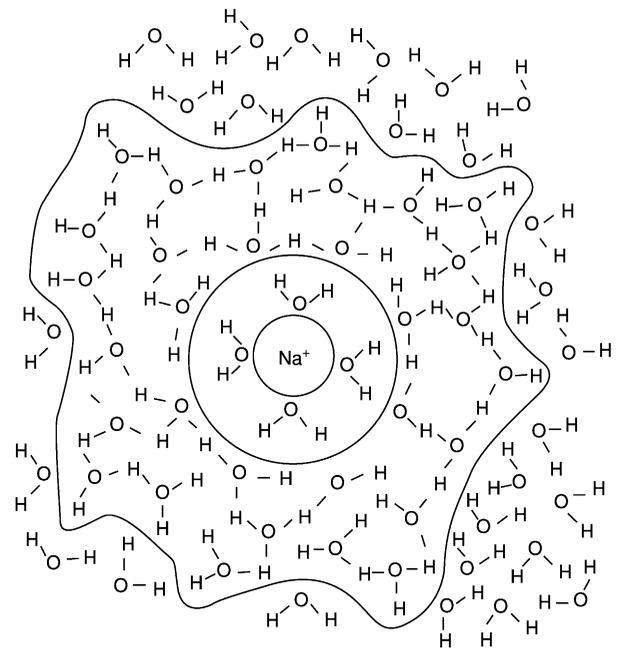


illustrated in **Figure 5**. In addition to hydration, there is also the hydrolysis of metal species, a reaction in which the metal ion displaces one of the protons (hydrogen) of water to form basic hydroxides.

Ion solvation is also aided by the tendency of the solvent to oppose the electrostatic attraction between ions of opposite charges. This is characterized by the dielectric constant  $D$ , which is defined by the relationship:

$$F = \kappa e_1 e_2 / D r^2 \quad [4]$$

Here  $F$  is the attractive force between two ions of opposite charge,  $\kappa$  is Coulomb's constant,  $e_1$  and  $e_2$  are charges on the ions, and  $r$  is the distance between them. Water has an extremely high dielectric constant, as shown in **Table 1**. For instance, the attractive force between  $Na^+$  and  $Cl^-$  ions at a given distance in water is less than one-third that in ethanol and only



**Figure 5** A model of the hydration 'atmosphere' of a sodium ion. An inner shell of more or less rigidly structured water is surrounded by a cluster of looser but still structure-enhanced water, the whole floating in a sea of 'free' water. Reprinted from *Environmental Soil Physics*, Hillel D (ed.). Copyright (1998), with permission from Elsevier.

**Table 1** Dielectric constants of some liquids (20°C)

Water	80	Acetone	21.4
Methanol	33	Benzene	2.3
Ethanol	24	Hexane	1.9

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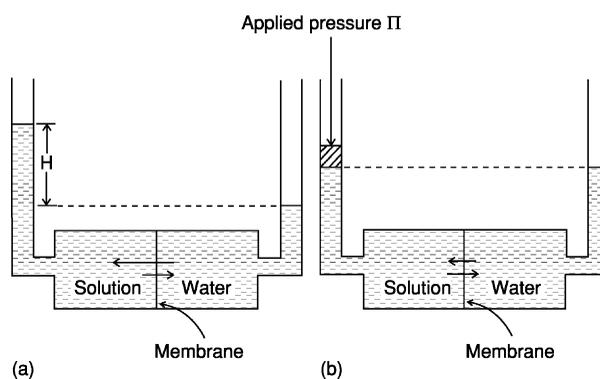
one-40th that in benzene. This fact greatly facilitates hydration of ions and dissolution of the crystal lattices of salts in water.

The effect of a solute on the solvent is manifest in a set of properties, namely, the colligative properties of solutions, which depend on the number of solute particles per unit volume of solvent. Solute particles produce such characteristic effects in the solvent as depression of the freezing point and of the vapor pressure, and elevation of the boiling point. They also endow a solution with the property of osmotic pressure. Theoretically, 1 mol of an ideal solute dissolved in 1 kg of water at a pressure of 760 mm of mercury (0.1 MPa, or 1 bar) depresses the freezing point by 1.86°C and elevates the boiling point by 0.543°C. Such a solution also yields an osmotic pressure of 2.24 MPa (22.4 atm) in an appropriate apparatus. However, aqueous solutions usually deviate considerably from ideal behavior, and the deviations are greater the higher the concentrations. The quantitative relationships given above are exact only at infinite dilution.

## Osmotic Pressure

Owing to the constant thermal motion of all molecules in a fluid (above a temperature of absolute zero), solute species spread throughout the solution in a spontaneous tendency toward a state of equal concentration throughout. This migration of solutes in response to spatial differences in concentration is called diffusion.

If a physical barrier is interposed between two regions, across the path of diffusion, and if that barrier is permeable to molecules of the solvent but not to those of the solute, the former will diffuse through the barrier in a process called osmosis (from the Greek *ωσμοσ*, meaning ‘push’). As in the case of unhindered diffusion, this process tends toward a state of uniform concentration even across the barrier. Barriers permeable to one substance in a solution but not to another are called selective or semipermeable membranes. Membranes surrounding cells in living organisms, for example, exhibit selective permeability to water while restricting the diffusion of solutes between the cells’ interior and their exterior environment. Water molecules cross the membrane in both directions, but the net flow of water is from the more dilute solution to the more concentrated.



**Figure 6** Osmosis and osmotic pressure: (a) in osmosis, the flow of water molecules through the membrane into the solutions is at first greater than the reverse flow from the solution into the water compartment. The hydrostatic pressure due to the column of expanded solution increases the rate of water flow from the solution to the water compartment until, at equilibrium, the opposite flows are equal. (b) The osmotic pressure of the solution is equal to the hydrostatic pressure  $\Pi$ , which must be applied to the solution to equalize the rate of flow to and from the solution and produce a net flow of zero. Reprinted from *Environmental Soil Physics*, Hillel D (ed.). Copyright (1998), with permission from Elsevier.

**Figure 6** is a schematic representation of a pure solvent separated from a solution by a semipermeable membrane. Solvent will pass through the membrane and enter the solution compartment, driving the solution level up the left-hand tube until the hydrostatic pressure of the column of dilute solution on the left is sufficient to counter the diffusion pressure of the solvent molecules drawn into the solution through the membrane. The hydrostatic pressure at equilibrium, when solvent molecules are crossing the membranes in both directions at equal rates, is the osmotic pressure of the solution.

In dilute solutions, the osmotic pressure is proportional to the concentration of the solution and to its temperature according to the following equation:

$$\Pi = MRT \quad [5]$$

Here  $\Pi$  is the osmotic pressure in atmospheres (to be multiplied by 0.101 to obtain megapascal units),  $M$  the total molar concentration of the solute (whether molecules or dissociated ions),  $T$  the temperature in degrees Kelvin, and  $R$  the gas constant (0.08205 liter atm deg<sup>-1</sup> mole). The osmotic pressure increase with temperature is associated with the corresponding increase of the molecular diffusivity (self-diffusion coefficient) of water,  $D_w$ . According to the Einstein–Stokes equation,

$$D_w = kT/6\pi\eta$$

where  $k = R/N$ , the Boltzmann constant ( $1.38 \times 10^{-23}$  JK<sup>-1</sup>);  $r$  is the rotation radius of the molecule ( $\sim 1.5 \times 10^{-4}$ ) and  $\eta$  is the viscosity.

## Solubility of Gases

The concentration of dissolved gases in water in equilibrium with a gaseous phase generally increases with pressure and decreases with temperature. According to Henry's law, the mass concentration of a dissolved gas  $c_m$  is proportional to the partial pressure of the gas  $p_i$ :

$$c_m = s_o p_i / p_o \quad [6]$$

where  $s_o$  is the solubility coefficient of the particular gas in water and  $p_o$  is the total pressure of the atmosphere. The volume concentration is similarly proportional:

$$c_v = s_v p_i / p_o \quad [7]$$

where  $s_v$  is the solubility coefficient expressed in terms of volume ratios (i.e.,  $c_v$  is the volume of dissolved gas relative to the volume of water). The values of  $s_c$  and  $s_v$  are determined experimentally. If the gas does not react chemically with the liquid, these properties should remain constant over a range of pressures, especially at low partial pressures of the dissolved gases. Solubility is, however, strongly influenced by temperature. Table 2 gives the  $s_v$  values of several atmospheric gases at various temperatures.

The solubilities of various gases (particularly oxygen) in varying conditions strongly influence such vital soil processes as oxidation and reduction, and respiration by roots and microorganisms.

## Adsorption of Water on Solid Surfaces

Adsorption is an interfacial phenomenon resulting from the differential forces of attraction or repulsion occurring among molecules or ions of different phases at their exposed surfaces. As a result of cohesive and adhesive forces coming into play, the zones of contact among phases may exhibit a concentration or a density of material different from that inside the phases themselves. As different phases come in contact, various types of adsorption can occur: adsorption of gases on solids, of gases on liquid surfaces, and of liquids on solids.

**Table 2** Solubility coefficients of gases in water

Temperature (°C)	Nitrogen (N <sub>2</sub> )	Oxygen (O <sub>2</sub> )	Carbon dioxide (CO <sub>2</sub> )	Air (without CO <sub>2</sub> )
0	0.0235	0.0489	1.713	0.0292
10	0.0186	0.0380	1.194	0.0228
20	0.0154	0.0310	0.878	0.0187
30	0.0134	0.0261	0.665	0.0156
40	0.0118	0.0231	0.530	—

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The interfacial forces of attraction or repulsion may themselves be of different types, including electrostatic or ionic (Coulombic) forces, intermolecular forces such as van der Waals and London forces, and short-range repulsive (Born) forces. The adsorption of water upon solid surfaces is generally of an electrostatic nature. The polar water molecules attach to the charged faces of the solids and to the ions adsorbed on them. This adsorption of water is the mechanism causing the strong retention of water by clay at high suctions.

The interaction of the charges of the solid with the polar water molecules may impart to the adsorbed water a distinct structure in which the water dipoles assume an orientation dictated by the charge sites on the solids. This adsorbed 'phase' may have mechanical properties of strength and viscosity that differ from those of ordinary liquid water at the same temperature. The adsorption of water on clay surfaces is an exothermic process, resulting in the liberation of an amount of heat known as the heat of wetting.

## Vapor Pressure

According to the kinetic theory, molecules in a liquid are in constant motion, which is an expression of their thermal energy. These molecules collide frequently, and occasionally one or another at the surface absorbs sufficient momentum to leap out of the liquid and into the atmosphere above it. Such a molecule, by virtue of its kinetic energy, thus changes from the liquid to the gaseous phase. This kinetic energy is then lost in overcoming the potential energy of intermolecular attraction while escaping from the liquid. At the same time, some of the randomly moving molecules in the gaseous phase may strike the surface of the liquid and be absorbed in it.

The relative rates of these two directions of movement depend upon the concentration of vapor in the atmosphere relative to its concentration at a state of equilibrium (i.e., when the movement in both directions is equal). An atmosphere that is at equilibrium with a body of pure water at standard atmospheric pressure is considered to be saturated with water vapor, and the partial pressure of the vapor in such an atmosphere is called the saturation (or equilibrium) vapor pressure. The vapor pressure at equilibrium with any body of water depends on the physical condition of the water (pressure and temperature) and its chemical condition (solutes) but is independent of the absolute or relative quantity of liquid or gas in the system.

The saturation vapor pressure rises with temperature. As the kinetic energy of the molecules in the liquid increases, so does the evaporation rate.

Consequently, a higher concentration of vapor in the atmosphere is required for the rate of return to the liquid to match the rate of escape from it. A liquid arrives at its boiling point when the vapor pressure becomes equal to the atmospheric pressure. If the temperature range is not too wide, the dependence of saturation vapor pressure on temperature is expressible by the equation (Table 3):

$$\ln p_o = a - b/T \quad [8]$$

where  $\ln p_o$  is the logarithm to the base  $e$  of the saturation vapor pressure  $p_o$ ,  $T$  is the absolute temperature, and  $a$  and  $b$  are constants.

As mentioned, the vapor pressure also depends on the hydrostatic pressure of the liquid water. At equilibrium with drops of water (which have a hydrostatic pressure greater than atmospheric), the vapor pressure is greater than in a state of equilibrium with free water (which has a flat interface with the atmosphere). On the other hand, in equilibrium with adsorbed or capillary water under a hydrostatic pressure smaller than atmospheric, the vapor pressure is smaller than in equilibrium with free water. The curvature of drops is considered to be positive, as these drops are convex toward the atmosphere, whereas the curvature of capillary water menisci is considered negative, as they are concave toward the atmosphere.

For water in capillaries, in which the air–water interface is concave, the Kelvin equation applies:

$$-(\mu_1 - \mu_1^o) = RT \ln (p_1^o/p_1) = 2\gamma v_1 \cos \alpha/r_c$$

in which  $(\mu_1 - \mu_1^o)$  is the change in potential of the water due to the curvature of the air–water interface,  $\gamma$  is the surface tension of water,  $\alpha$  is the contact

angle,  $v_1$  is the partial molar volume of water, and  $r_c$  is the radius of the capillary.

Water present in the soil invariably contains solutes, mainly electrolytic salts, in variable concentrations. Thus, soil water should properly be called the soil solution. The composition and concentration of the soil solution affect soil behavior. While in humid regions the soil solution may have a concentration of but a few parts per million, in arid regions the concentration may become as high as several percent. The ions commonly present are  $H^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $NH_4^+$ ,  $OH^-$ ,  $Cl^-$ ,  $HCO_3^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ , and  $CO_3^{2-}$ . The vapor pressure of electrolytic solutions is less than that of pure water. The equation is:

$$v_1 \Pi_o = RT \ln (p_1^o/p_1) = \mu_1 - \mu_1^o$$

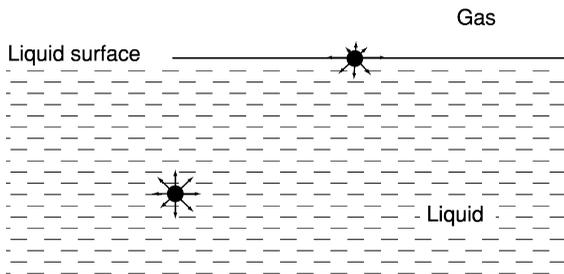
wherein  $\Pi_o$  is the osmotic pressure of a nonvolatile solute,  $\mu_1^o$  and  $p_1^o$  are the chemical potential and vapor pressure of the liquid in its pure state, and  $\mu_1$  and  $p_1$  are the same for the solution. Thus the soil solution has a lower vapor pressure than pure water, even when the soil is saturated. In unsaturated soil the capillary and adsorptive effects further lower the potential and hence also the vapor pressure.

## Surface Tension

Surface tension is a phenomenon occurring typically, but not exclusively, at the interface of a liquid and a gas. The liquid behaves as if it were covered by an elastic membrane in a constant state of tension that tends to cause the surface to contract. To be sure, no such membrane exists, yet the analogy is a useful one if not taken too literally. If we draw an arbitrary line of length  $L$  on a liquid surface, there will be a force  $F$

**Table 3** Physical properties of water vapor

Temperature (°C)	Saturation vapor pressure (torr)		Vapor density in saturated air (kg m <sup>-3</sup> )		Diffusion coefficient (m <sup>2</sup> s <sup>-1</sup> ) (× 10 <sup>-4</sup> )
	Over liquid	Over ice	Over liquid (× 10 <sup>-3</sup> )	Over ice (× 10 <sup>-3</sup> )	
-10	2.15	1.95	2.36	2.14	0.211
-5	3.16	3.01	3.41	3.25	—
0	4.58	4.58	4.85	4.85	0.226
5	6.53	—	6.80	—	—
10	9.20	—	9.40	—	0.241
15	12.78	—	12.85	—	—
20	17.52	—	17.30	—	0.257
25	23.75	—	23.05	—	—
30	31.82	—	30.38	—	0.273
35	42.20	—	39.63	—	—
40	55.30	—	51.1	—	0.289
45	71.90	—	65.6	—	—
50	92.50	—	83.2	—	—



**Figure 7** Cohesive forces acting on a molecule inside the liquid and at its surface.

pulling the surface to the right of the line and an equal force pulling the surface leftwards. The ratio  $F/L$  is the surface tension and its dimensions are those of force per unit length. The same phenomenon can also be described in terms of energy. Increasing the surface area of a liquid requires work, which remains stored as potential energy in the enlarged surface, just as energy can be stored in a stretched spring. That potential energy can perform work if the enlarged surface is allowed to contract again. Energy per unit area has the same dimensions as force per unit length.

An explanation for occurrence of surface tension is given in **Figure 7**. A molecule inside the liquid is attracted in all directions equally by the cohesive forces of neighboring molecules, while a molecule at the surface of the liquid is attracted into the relatively dense liquid phase by a net force greater than that attracting it toward the rarified gaseous phase. This unbalanced force draws the surface molecules inward into the liquid and results in the tendency for the surface to contract. This is why drops of a liquid in air as well as bubbles of air in a liquid assume the shape of a sphere, which is a body of minimal surface exposure relative to its volume.

Different liquids exhibit different surface tension values, as in the following list:

Water,  $7.27 \times 10^{-2} \text{ N m}^{-1}$  ( $72.7 \text{ dyn cm}^{-1}$ ) at  $20^\circ\text{C}$ ;  
 Ethyl ether,  $1.7 \times 10^{-2} \text{ N m}^{-1}$  ( $17 \text{ dyn cm}^{-1}$ );  
 Ethyl alcohol,  $2.2 \times 10^{-2} \text{ N m}^{-1}$  ( $22 \text{ dyn cm}^{-1}$ );  
 Benzene,  $2.9 \times 10^{-2} \text{ N m}^{-1}$  ( $29 \text{ dyn cm}^{-1}$ );  
 Mercury,  $0.43 \text{ N m}^{-1}$  ( $430 \text{ dyn cm}^{-1}$ ).

### Curvature of Water Surfaces and Hydrostatic Pressure

Wherever an interface between fluids (say, between water and air) is not planar but curved, the resolution of forces due to surface tension creates a pressure differential across that interface. For a spherical interface (as in the case of a bubble of air immersed in a body of water), the pressure difference is proportional

#### BOX 1 A Farewell to Teardrops

For centuries, conventional wisdom held that larger stones fall faster than small ones, that the Earth is flat yet the sun revolves around it, and that the sun and moon are of equal size. We would like to believe that in our time all baseless notions have been replaced by sound science. But have they?

Consider the shape of a raindrop. The conventional standard is a teardrop, rounded at the bottom and tapering to a point at the top. So prevalent is that image that it is printed in textbooks and used as a logo by irrigation companies and even by conferences sponsored by the United Nations. Alas, the vertically elongated, top-pointed raindrop is a physical impossibility.

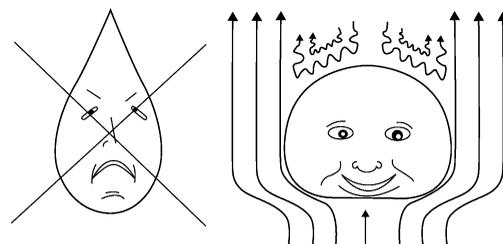
A drop forming at the tip of a spout assumes that shape only at the very instant of detachment. Because of surface tension, any drop suspended in air 'balls up' spontaneously into a sphere. In a cloud, spherical droplets tend to grow by condensation or coalescence until reaching a critical weight, at which they begin to fall.

Air bypassing a falling drop acquires greater velocity around the curved 'waist' of the drop than near its top or bottom. By Bernoulli's law ( $p + \rho v^2/2 = \text{constant}$ ), the pressure of the air alongside the drop is lowered relative to that of the air above and below the drop. Consequently the drop compresses vertically and comes to resemble an ellipsoid. Such is indeed the shape of small drops ( $< 2 \text{ mm}$ ).

In the case of larger drops, the laminar streams of air flowing past the drop may not converge smoothly above the top, but may leave a turbulent wake there. In such a wake, the pressure is lower than it would be in an ideally laminar flow regime. The reduced air pressure at the top causes the drop to bulge a bit there, thus acquiring the appetizing shape of a miniature hamburger bun (described by the appropriately named McDonald as early as 1954).

If a drop were to continue accelerating, it might eventually spread out to form a pancake. But Stokes' law intervenes, decreeing that the drop's acceleration be countered by the increasing viscous resistance of the air. When air resistance equals the gravitational force, acceleration ceases and the drop continues to fall at a constant 'terminal' velocity and with a more or less constant shape. It finally slaps the ground with its flattened face going 'plop'.

Some of us may think it unfair that such an exquisitely sculpted natural body should have no more glorious a fate than to splatter down on some dry bit of earth. But that is where – having at once lost its distinctive shape as it enters the labyrinthine interstices of the soil – our drop might well give life to a thirsty plant, perhaps even to a sunflower. Anyway, we bid farewell to the sad countenance of the teardrop, a singularly inappropriate symbol for happy rain.



**Figure B1** Conventional and real raindrops. Reprinted from *Environmental Soil Physics*, Hillel D (ed.). Copyright (1998), with permission from Elsevier.

to the surface tension and inversely proportional to the curvature:

$$\Delta P = 2\gamma/R \quad [9]$$

Thus, the smaller the bubble is, the greater is its pressure.

If the bubble is not spherical, then instead of eqn [9] we obtain:

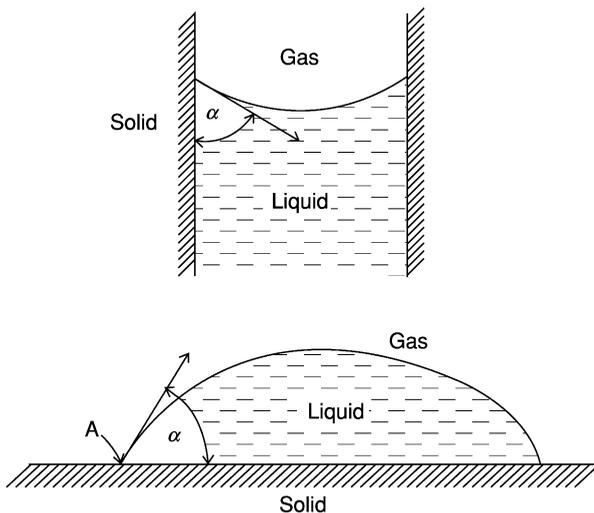
$$\Delta P = \gamma(1/R_1 + 1/R_2) \quad [10]$$

where  $R_1$  and  $R_2$  are the principal radii of curvature for any given point on the interface. Eqn [10] reduces to [9] whenever  $R_1 = R_2$ .

### Contact Angle of Water on Solid Surfaces

If we place a drop of liquid upon a dry solid surface, the liquid will usually displace the gas that covered the surface of the solid and it will spread over that surface to a certain extent. Where its spreading ceases and the edge of the drop comes to rest, it will form a typical angle with the surface of the solid. This angle, termed contact angle, is illustrated in Figure 8.

We now consider what factors determine the magnitude of the angle  $\alpha$ . We can expect that angle to be acute if the adhesive affinity between the solid and liquid is strong relative to the cohesive forces inside the liquid itself and to the affinity between the gas and the solid. We can then say that the liquid 'wets' the solid. A contact angle of zero would mean the complete flattening of the drop and the perfect wetting of the solid surface by the liquid. On the other hand, a contact angle of  $180^\circ$  would imply a complete non-wetting or rejection of the liquid by the gas-covered



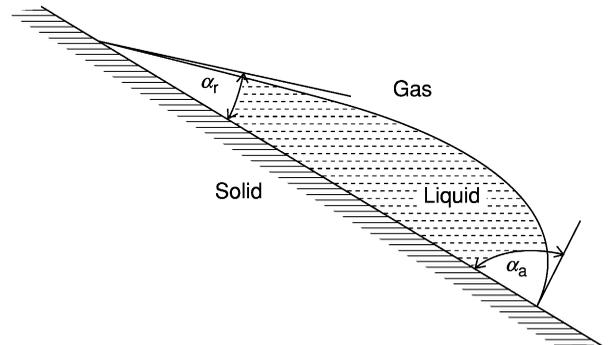
**Figure 8** The contact angle of a meniscus in a capillary tube and a drop resting on the surface of a solid. Reprinted from *Environmental Soil Physics*, Hillel D (ed.). Copyright (1998), with permission from Elsevier.

solid. In that case the drop would retain its spherical shape without spreading over the surface at all (assuming no gravity effect). Surfaces on which water exhibits an obtuse contact angle are called water-repellent, or hydrophobic (Greek: 'water-hating').

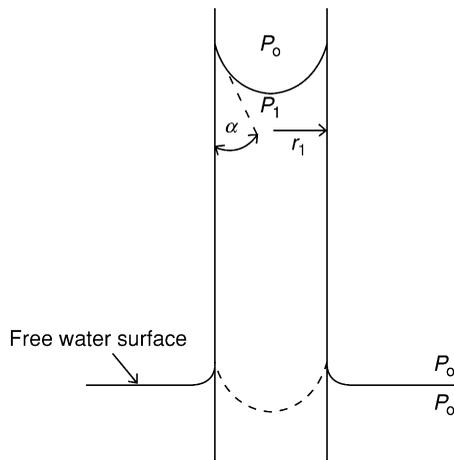
The contact angle of a given liquid on a given solid is generally characteristic of its interaction under given physical conditions. This angle, however, may be different in the case of a liquid that is advancing over the solid surface than in the case of the same liquid receding over the surface. This phenomenon, where it occurs, is called contact angle hysteresis. The wetting angle of pure water upon clean and smooth mineral surfaces is generally zero, but where the surface is rough or coated with adsorbed surfactants of a hydrophobic nature, the contact angle, and especially the wetting angle, can be considerably greater than zero. This is illustrated in Figure 9.

### The Phenomenon of Capillarity

A capillary tube dipped in a body of free water will form a meniscus as the result of the contact angle of water with the walls of the tube. The curvature of this meniscus will be greater (i.e., the radius of curvature smaller) the narrower the tube. The occurrence of curvature causes a pressure difference to develop across the liquid-gas interface. A liquid with an acute contact angle (e.g., water on glass) will form a concave meniscus, and therefore the liquid pressure under the meniscus ( $P_1$ ) will be smaller than the atmospheric pressure (Figure 10). Hence, the water inside the tube will be driven up the tube from its initial location (shown as a dashed curve in Figure 10) by the greater pressure of the free water (i.e., water at atmospheric pressure, under a horizontal air-water interface) outside the tube at the same level. The



**Figure 9** Hypothetical representation of a drop resting on an inclined surface. The contact angle  $\alpha_a$ , at the advancing edge of the drop, is shown to be greater than the corresponding angle  $\alpha_r$  at the receding edge. Reprinted from *Environmental Soil Physics*, Hillel D (ed.). Copyright (1998), with permission from Elsevier.



**Figure 10** Capillary rise. Reprinted from *Environmental Soil Physics*, Hillel D (ed.). Copyright (1998), with permission from Elsevier.

upward movement will stop when the pressure difference between the water inside the tube and the water under the flat surface outside the tube is countered by the hydrostatic pressure exerted by the water column in the capillary tube.

If the capillary tube is cylindrical and if the contact angle of the liquid on the walls of the tube is zero, the meniscus will be a hemisphere (and in a two-dimensional drawing can be represented as a semicircle) with its radius of curvature equal to the radius of the capillary tube. If, on the other hand, the liquid contacts the tube at an angle greater than zero but smaller than 90°, then the diameter of the tube (2r) is the length of a cord cutting a section of a circle with an angle of  $\pi - 2\alpha$ , as shown in **Figure 11**. Thus,

$$R = r / \cos \alpha \quad [12]$$

where R is the radius of curvature of the meniscus, r the radius of the capillary, and  $\alpha$  the contact angle.

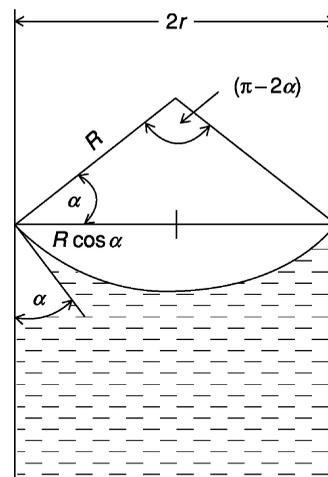
The pressure difference  $\Delta P$  between the capillary water (under the meniscus) and the atmosphere, therefore, is:

$$\Delta P = (2\gamma \cos \alpha) / r \quad [13]$$

Recalling that hydrostatic pressure is proportional to the depth  $d$  below the free water surface (i.e.,  $P = \rho g d$ , where  $\rho$  is liquid density and  $g$  is gravitational acceleration) we can infer that hydrostatic tension (negative pressure) in a capillary tube is proportional to the height  $h$  above the free water surface. Hence the height of capillary rise is:

$$h_c = (2\gamma \cos \alpha) / g(\rho_l - \rho_o)r \quad [14]$$

where  $\rho_g$  is the density of the gas (which is generally neglected),  $\rho_l$  the density of the liquid,  $g$  the



**Figure 11** The geometric relationship of the radius of curvature R to the radius of the capillary r and the contact angle  $\alpha$ . Reprinted from *Environmental Soil Physics*, Hillel D (ed.). Copyright (1998), with permission from Elsevier.

acceleration of gravity, r the capillary radius,  $\alpha$  the contact angle, and  $\gamma$  the surface tension between the liquid and the air.

When the liquid surface is concave, the center of curvature lies outside the liquid and the curvature, by convention, is regarded as negative. Thus, for a concave meniscus such as that of water in a clean glass capillary,  $\Delta P$  is negative with reference to the atmosphere, indicating a capillary pressure deficit, or subpressure, called tension. On the other hand, in a capillary tube that forms a convex meniscus (such as that of mercury in glass, or of water in an only or otherwise water-repellent tube),  $\Delta P$  is positive and capillary depression, rather than capillary rise, will result.

### Density and Compressibility

The open packing of water molecules in ice and liquid water accounts for their relatively low densities. Unlike most substances, water exhibits a point of maximum density (at 4°C), below which the substance expands due to the formation of a hexagonal lattice structure, and above which the expansion is due to the increasing thermal motion of the molecules. The coefficient of thermal expansion of water is rather low, and in the normal temperature range of, say, 4–50°C, the density diminishes only slightly, from 1000 to 988 kg m<sup>-3</sup>.

The compressibility of water,  $C_w$ , can be defined as the relative change in density with change in pressure:

$$C_w = (1/\rho_w)(d\rho_w/dP) \quad [15]$$

At 20°C and at atmospheric pressure, the compressibility of pure water is about  $4.6 \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$ . In

**Table 4** Physical properties of liquid water

Temperature (°C)	Density(kg m <sup>-3</sup> ) (× 10 <sup>3</sup> )	Specific heat (J kg <sup>-1</sup> deg) (× 10 <sup>3</sup> )	Latent heat (vaporization) (J kg <sup>-1</sup> ) (× 10 <sup>6</sup> )	Surface tension (kg s <sup>-2</sup> ) (× 10 <sup>-2</sup> )	Thermal conductivity (J m <sup>-6</sup> s deg)	Dynamic viscosity (kg m <sup>-1</sup> s) (× 10 <sup>-2</sup> )	Kinematic viscosity (m <sup>2</sup> s <sup>-1</sup> ) (× 10 <sup>-6</sup> )
-10	0.99794	4.27	2.53	—	—	—	—
-5	0.99918	4.23	2.51	7.64	—	—	—
0	0.99987	4.22	2.50	7.56	0.561	0.1787	1.79
4	1.00000	4.21	2.49	7.5	0.570	0.1567	1.57
5	0.99999	4.207	2.49	7.48	0.574	0.1519	1.52
10	0.99973	4.194	2.48	7.42	0.587	0.1307	1.31
15	0.99913	4.19	2.47	7.34	0.595	0.1139	1.14
20	0.99823	4.186	2.46	7.27	0.603	0.1002	1.007
25	0.99708	4.18	2.44	7.19	0.612	0.0890	0.897
30	0.99568	4.18	2.43	7.11	0.620	0.0798	0.804
35	0.99406	4.18	2.42	7.03	0.629	0.0719	0.733
40	0.99225	4.18	2.41	6.95	0.633	0.0633	0.661
45	0.99024	4.18	2.40	6.87	0.641	0.0596	0.609
50	0.98807	4.186	2.38	6.79	0.645	0.0547	0.556

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the normal situations encountered on the surface of the Earth, water can usually be considered incompressible. The compression of water cannot be ignored, however, in the case of deep confined aquifers, which may be subject to a pressure of, say, 10 MPa or more.

### Dynamic and Kinematic Viscosity

When a fluid is moved in shear (i.e., when adjacent layers of fluid are made to slide over each other), the force required is proportional to the velocity of shear. The proportionality factor is called the viscosity. As such, it is the property of the fluid to resist the rate of shearing and this can be visualized as an internal friction. The coefficient of viscosity  $\eta$  is defined as the force per unit area necessary to maintain a velocity difference of 1 m s<sup>-1</sup> between two parallel layers of fluid which are 1 m apart. The viscosity equation is:

$$\tau = F_s/A = \eta \, du/dx \quad [16]$$

wherein  $\tau$  is the shearing stress, consisting of a force  $F_s$  acting on an area  $A$ ;  $\eta$  (dimensions: mass/(length × time)) is the coefficient of dynamic viscosity; and  $du/dx$  is the velocity gradient perpendicular to the stressed area  $A$ .

The ratio of the dynamic viscosity of a fluid to its density is called the kinematic viscosity, designated

$\nu$ . It expresses the shearing-rate resistance of a fluid independently of the density. Thus, while the dynamic viscosity of water exceeds that of air by a factor of about 50 (at room temperature), its kinematic viscosity is actually lower.

Fluids of lower viscosity flow more readily and are said to possess greater fluidity (which is the reciprocal of viscosity). As shown in [Table 4](#), the viscosity of water diminishes by over 2% per 1°C rise in temperature, and thus decreases by more than half as the temperature increases from 5 to 35°C. The viscosity is also affected by the type and concentration of solutes present.

*See also:* **Capillarity; Hydrodynamics in Soils; Water Cycle**

### Further Reading

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